

Environmental Health and Hazard Risk Assessment

Principles and Calculations

Louis Theodore
R. Ryan Dupont



CRC Press
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Taylor & Francis Group
Boca Raton London New York

CRC Press is an imprint of the
Taylor & Francis Group, an **informa** business

CRC Press
Taylor & Francis Group
6000 Broken Sound Parkway NW, Suite 300
Boca Raton, FL 33487-2742

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Version Date: 20120502

International Standard Book Number-13: 978-1-4398-6888-1 (eBook - PDF)

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To

Frankie

a very special student and now colleague

who helped make my last 2 years at MC

exciting, productive, and professionally rewarding

Lou Theodore

Sonia and the cats and kids, who make this all worthwhile.

R. Ryan Dupont

He that publishes a book runs a very great hazard since nothing can be more impossible than to compose one that may secure the approbation of every reader.

Miguel DeCervantes (1547–1616)
Don Quixote, Part I, Book III, Chapter 3, 446

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Preface

And I honor the man who is willing to sink
Half his present repute for the freedom to think,
And, when he has thought, be his cause strong or weak,
Will risk t' other half for the freedom to speak.

James R. Russell (1819–1891)
A Fable for Critics

Risk. Health risk. Hazard risk. Individual risk. Societal risk. Etc. Risk has surged to the forefront of numerous engineering and scientific areas of interest. Why? A good question. Some of the more obvious reasons include (not in the order of importance) the following:

1. Increased environmental health and safety legislation
2. The accompanying massive regulations
3. Regulatory fines
4. Liability concerns
5. Environmental activists and their organizations
6. Public concerns
7. Skyrocketing health-care costs
8. Skyrocketing workers' compensation costs
9. Codes of ethics

These factors, individually or *in toto*, have created a need for engineers and scientists to develop a proficiency in risk and risk-related areas. In turn, this need has given rise to the driving force that led to the writing of this book. Specific details follow.

Society has indeed experienced the aforementioned dramatic explosion (no pun intended) in technological advances that continue to accelerate. These advances include new domestic products, new drugs, sophisticated industrial processes, energy exploration and development, and expansion into outer space, all of which have introduced (particularly in the workplace) new diseases, have complicated numerous earlier health-related problems, and have caused unanticipated accidents.

The rapid growth and expansion of the chemical and petroleum industry have been accompanied by a simultaneous rise in both human health problems and human, material, and property losses because of fires, explosions, hazardous and toxic spills, equipment failures, other accidents, and

business interruptions. Concern over the potential consequences of massive emissions of “harmful” chemicals and catastrophic accidents, particularly at chemical and petrochemical plants, has sparked interest at both the industrial and regulatory levels in obtaining a better understanding of the subject of this book, *Environmental Health and Hazard Risk Assessment: Principles and Calculations*. The writing of this book was also undertaken, in part, as a result of this growing concern.

In the wake of the British Petroleum (BP) Deepwater Horizon offshore oil rig explosion on April 20, 2010, and the accompanying millions of gallons of oil that were released into the Gulf of Mexico from the damaged rig, the general subject of environmental risk suddenly took on a never-dreamed-of level of importance at the national level. How and why this disaster occurred is still being debated by engineers, scientists, politicians, regulators, and the average citizen. One thing that cannot be debated is that the BP rig catastrophe produced the worst environmental disaster in American history. Officials of not only BP but also Exxon Mobil, Conoco Phillips, Shell, and Chevron continue to insist that the accident was an aberration and could not happen again. Really? The scientific community knows better since accidents are an integral part of life; discussions of this nature have to ultimately lead to an often-misunderstood term referred to as “risk.”

The subject of emergency preparedness and response has also surfaced. Immediately following the BP disaster, steps were taken not only to prepare for the environmental effects associated with the massive emission that occurred but also to institute programs and actions to help reduce (or possibly eliminate) the probability of this occurring again. For example, the oil from the blown-out deepwater well had the potential to move up the Atlantic coast and ultimately reach Long Island (home to one of the authors), beaches, and local estuaries. Nassau County worked with New York City in tracking the currents of the spill at the time. In addition to tracking that spill, the County was in partnership with other municipalities in drafting an oil spill response plan to address any local impacts.

In recent years, the engineering profession has expanded its responsibilities to society to include environmental risk, with particular emphasis on accidents and massive emissions arising at industrial sources. Increasing numbers of engineers, scientists, technicians, and maintenance personnel are now confronting problems in this most important area. To cope with these challenges, the engineers and scientists of today and tomorrow must develop both a proficiency in environmental risk and an improved understanding of the subject. Because environmental risk is a highly sophisticated and complex endeavor, many company administrators and regulatory officials are seeking highly trained and professionally educated personnel to fill positions in this area. Thus, companies and government agencies have acquired an interest in the continuing education of employees and students. It was also in the spirit of responding to this particular concern that this book was undertaken.

Regarding students, the Accreditation Board for Engineering and Technology (ABET) requires that engineering graduates understand the engineer's responsibility to protect both the public and workers' safety. Traditionally, engineering schools have done an excellent job of educating their students on the fundamental laws of nature governing their fields and on the application of these laws to the solution of engineering problems. Unfortunately, they have been less successful in conveying to the students the importance of occupational health and environmental safety in the design of chemical processes. This concern also served as a driving force for the writing of this book.

This book is intended primarily for regulatory officials, company administrators, engineers, technicians, industry maintenance personnel, and both undergraduate and first-year graduate students. It is assumed that the reader has taken basic courses in physics and chemistry; only a minimum background in mathematics is required (though calculus is desirable). Our aims are to offer the reader the fundamentals of health risk and hazard risk assessment with appropriate practical applications in the chemical process industries, and to provide an introduction to the specialized and reference books in this and related areas. The reader is encouraged to use the works cited in the bibliography to continue development beyond the scope of this book.

As is usually the case in preparing a manuscript, the decisions of what to include and what to omit have been difficult. However, every attempt has been made to offer engineering and science course material to readers at a level that will enable them to better cope with some of the complex problems encountered in this field.

This book is divided into four parts. Part I (Introductory Comments) serves as an introduction to the book and presents both legal considerations and emergency planning and response. This part basically serves as an overview to the more technical topics covered in the remainder of the book. Part II (Health Risk Assessment) treats the broad subject of health risk assessment while discussing toxicology, exposure, and health risk characterization. Part III (Hazard Risk Assessment) examines hazard risk assessment in significant detail. The five chapters in this part include materials on problem identification, probability, consequence, and characterization of hazards/accidents, as well as the fundamentals of applicable statistics theory. The applications and calculations of risk analysis for real systems are treated in Part IV (Case Studies) with the presentation of four case studies concerned with

1. Monte Carlo simulation
2. Emergency planning and response
3. Natural disasters
4. Industrial accidents

For some readers, particularly students, the book may serve as a starting point that will allow them to become acquainted with the environmental risk assessment field. For others who would classify themselves as experts, the book could serve as a reference book. It may also be useful as a tool for training in industry, government, or academia. The book should be valuable to engineers in agencies and industry, to technicians, and to maintenance personnel. It may also be of value to individuals involved with the general field of environmental management. Our aim is to provide, in a thorough and clear manner, a book covering both the fundamentals of health, safety, and accident management and their application to real-world problems. It is hoped that it will serve both industry and government (as well as academia) in attempting to reduce and/or eliminate environmental health effects and accidents that can result in the loss of human and animal life, materials, vegetation, and property.

During the preparation of this book, we were ably assisted in many ways by a number of Manhattan College graduate students and practicing engineers with expertise in this field. We gratefully acknowledge the contributors to the first-generation John Wiley (1989) book titled *Accident and Emergency Management* and the second-generation Marcel Dekker (1995) reference book titled *Accident and Emergency Management in the Chemical Process Industries*. They include

Chapter 1: Past history—John O’Byrne

Chapter 2: Legislation—Gaetano LaVigua

Chapter 3: Emergency planning and response—Elizabeth Shoen

Chapter 5: Fires, explosions and other accidents—Nat Federici and
Isabella Schroeder

Chapter 6: Accident prevention in process facilities—Carol Earle (Conti)

Chapter 7: Process applications—Anthony Gardetto and Chassam
Koderska

The following author contributed only partially:

Chapter 4: Process fundamentals and plant equipment—Michael Venezia.

Drs. Joseph Reynolds and Frank Taylor served as coauthors (with Dr. Theodore) for the Wiley book while Dr. Ann Marie Flynn coauthored (with Dr. Theodore) the Marcel Dekker book. In addition, several illustrative examples and problems were drawn, in part, from the contributions of several faculty who participated in an earlier National Science Foundation-funded College Faculty Workshop that was conducted at Manhattan College.

Last, but not least, we believe that this modest work will help the majority of individuals working in the environmental field to obtain a reasonably complete understanding of both health risk and hazard risk assessment. If you have come this far and read through the preface, you have more than

just a passing interest in this subject. We strongly suggest you try this book; we think you will like it.

Lou Theodore

R. Ryan Dupont

Note: This book also provides a useful resource in the form of a CRC Press website, <http://www.crcpress.com/product/isbn/9781439868874>, which contains over 150 additional problems and 15 hours of exams; *solutions* for these problems and exams are available for those who *adopt* the book for training and/or academic purposes.

Introduction

This book is primarily concerned with health risk and hazard risk assessment calculations. Unfortunately, these two classes of environmental risks have come to mean different things to different people.

For the readers, it should be noted that health risk addresses risks that arise from health and health-related problems. Chemicals are generally the culprit. Both the effect on and exposure to a receptor (in this case, generally a human) ultimately determine the risk to the individual for the health problem of concern. The risk can be described in either qualitative or quantitative terms, and there are various terms that may be used, e.g., 10 individuals will become sick, or 1×10^{-6} (one in a million) will die, or something as simple as "it is a major problem."

The second category of environmental risk is hazard risk. This class of risk is employed to describe risks associated with hazards or hazard-related problems, e.g., accidents, negative events, and catastrophes. Unlike most health problems, these usually occur over a short period of time, e.g., seconds or minutes. Both the probability and the consequence associated with the accident/event ultimately determine the hazard risk. Once again, the risk can be described in either qualitative or quantitative terms, and there are various terms that may be used.

Once a risk has been calculated, one needs to gauge the estimated consequences (or opportunities if examining financial/economic scenarios) and evaluate and prioritize options for risk management or mitigation. These potentially strategic evaluations are usually fraught with uncertainties at numerous levels. Thus, the risk assessment process is normally followed by option analyses; these options can be based on decision-making procedures that are beyond the scope of this book. However, it is fair to say that there may be a full range of outcomes and consequences to various scenarios. It should also be noted that risk assessment is a dynamic process that can very definitely be a function of time. Much of the material in this paragraph is addressed in the book, but some receives superficial treatment.

Environmental risk is one type of risk. Although this book primarily addresses this class of risk, there are others. Consider, for example, financial risk that can arise in the chemical process industry. The cost of the capital of a proposed new venture is primarily dependent on three factors: (1) the proportion of equity to debt financing, (2) the method of financing involved, and (3) the risk inherent in the proposed project. As with environmental risk, uncertainties abound in these economic analyses. Discounted cash flow rates of return or net present values for these projects can rarely be predicted with absolute certainty because of a host of factors. This topic is also beyond the scope of this book.

Since emergency planning and response to both health and hazard problems are two topics directly related to environmental risk, they too are covered in this book. Although these two subjects are primarily concerned with hazards, they can—and often do—play an important role in any comprehensive environmental risk analysis.

The material to follow—all four parts—attempts to examine the aforementioned topic areas in a clear and comprehensive manner. Essay material is complemented with numerous illustrative examples, many of which have been drawn from real-world experiences and applications.

Part I

Introductory Comments

It is better to risk saving a guilty person than to condemn an innocent one.

Voltaire (Francois Marie Arouet) (1694–1778)

Zadig [1747], Chapter 6

1

About the Book

1.1 Introduction

The rapid growth and expansion of the chemical and energy industry has been accompanied by not only a spontaneous rise in chemical emissions to the environment but also human, material, and property losses because of fires, explosions, hazardous and toxic spills, equipment failures, other accidents, and business interruptions. Concern over the potential consequences of these massive emissions and catastrophic accidents, particularly at chemical, petrochemical, and utility plants, has sparked interest at both the industrial and regulatory levels in obtaining a better understanding of the main subject of this book: *Environmental Health and Hazard Risk Assessment: Principles and Calculations*. The writing of this “risk” book was undertaken, in part, as a result of this growing concern.

Risk of all types (health risk, hazard risk, individual risk, societal risk, etc.) has surged to the forefront of numerous engineering and science areas of interest. Why? A good question. Some of the more obvious reasons include (not in the order of importance) the following:

1. Increased environmental health and safety legislation
2. The accompanying massive regulations
3. Regulatory fines
4. Liability concerns
5. Environmental activists and their organizations
6. Public concerns
7. Skyrocketing health care costs
8. Skyrocketing workers’ compensation costs
9. Codes of ethics

These factors, individually or *in toto*, have created a need for engineers and scientists to develop a proficiency in risk and risk-related topics. In turn, this need gave rise to the driving force that led to the writing of this book.

Members of society are confronted with risks on a daily basis. Here is a sampling of some activities for which risk can play a role:

1. Electrocution when turning on the TV
2. Using soap with chemical additives
3. Tripping down stairs
4. Drinking Starbucks coffee
5. Driving to work
6. Eating a hot dog for lunch
7. Being struck by an automobile while returning from lunch

Risks abound. They are all around us and society has little to no control over many of them. Perhaps a careful analysis of risks is in order.

Health problems and accidents can also occur in many ways other than from routine, daily, “normal” activities. There may be a chemical spill, a round-the-clock emission from a power plant, an explosion, or a runaway reaction in a nuclear plant. There are also potential risks and accidents in the transport of people and materials: trucks overturning, trains derailling, ships capsizing, etc. There are “acts of God” such as earthquakes, tsunamis, and tropical storms. It is painfully clear that health and hazard problems are a fact of life. The one common thread through all of these situations is that these problems are rarely understood and, unfortunately, they are frequently mismanaged.

The job of the engineer and scientist is to measure or calculate the magnitude of risk and often compare the magnitude of one risk to other risks that are similar in nature. Perhaps more difficult is the task of comparing the risk of one event with risks arising from events of a totally different nature.

Topics addressed in this chapter include:

Why use risk-based decision making?

Definitions

Risk terms

Financial risk

1.2 Why Use Risk-Based Decision Making?

The use of a risk-based decision-making process allows for efficient allocation of limited resources such as time, money, regulatory oversight, and qualified professionals. Advantages of using this process include the following:

1. Decisions are based on reducing the risk of adverse human or environmental impacts.
2. Data collection activities are focused on collecting only that information that is necessary to make risk-related decisions.
3. Limited resources are focused on those sites or scenarios that pose the greatest risk to human health and the environment.
4. Compliance or risk mitigation effectiveness can be evaluated relative to site-specific standards or goals.
5. More cost-effective risk mitigation may be achieved, oftentimes more rapidly, than is normally possible.

By using risk-based decision making, decisions are made in a consistent manner. Protection of both human health and the environment is accounted for.

A variety of U.S. Environmental Protection Agency (EPA) programs involved in the protection of groundwater and cleanup of environmental contamination utilize the risk-based decision-making approach. Under the EPA's regulations dealing with the cleanup of underground storage tank (UST) sites, regulators are expected to establish goals for cleanup of UST releases based on consideration of factors that could influence human and environmental exposure to contamination. Where UST releases affect the groundwater being used as public or private drinking water sources, EPA generally recommends that cleanup goals be based on health-based drinking water standards. Even in such cases, however, risk-based decision making can be employed to focus on corrective action.

In the Superfund program (see Chapter 5), risk-based decision making plays an integral role in determining whether a hazardous waste site belongs on the National Priorities List. Once a site is listed, qualitative and quantitative risk assessments are used as the basis for establishing the need for action and for identifying remedial alternatives. To simplify and accelerate baseline risk assessments at Superfund sites, EPA has developed generic soil screening guidance that can be used to help distinguish between contamination levels that generally present no health concerns and those that generally require further evaluation. The Resource Conservation and Recovery Act (RCRA) Corrective Action Program also uses risk-based decision making to set priorities for cleanup so that high-risk sites receive attention as quickly as possible to assist in the determination of cleanup standards and to prescribe management requirements for remediation of wastes.

It should be noted that disasters and accidents in the past have become the driving force for innovation from a risk perspective. The trial-and-error process associated with the development of the chemical, petrochemical, space, nuclear, etc., industries have unfortunately resulted in the loss of an untold number of lives. Failure has never been desirable. But failures, often appalling and inevitable, almost always have assisted engineers

and scientists in preventing future, potentially more catastrophic failures. In effect, much of today's technological development can be attributed to failures that society often chooses to forget. Hopefully, the recent BP offshore oil rig disaster, to be discussed in Chapters 3, Chapter 21, and Case Study 4, will lead to additional and more meaningful technological advancements in deep water offshore oil drilling.

1.3 Book Contents

As is usually the case in preparing a manuscript on risk, the decisions of what to include and what to omit have been difficult. However, every attempt has been made to offer engineering and science (course) material to readers at a level that will enable them to better cope with some of the complex problems encountered in this field.

This book is divided into four parts: Introductory Comments, Health Risk Assessment, Hazard Risk Assessment, and Case Studies. Part I, an introduction to health risk and hazard risk, presents regulatory considerations, emergency planning, and emergency response. This part basically serves as an overview to the more technical topics covered in the remainder of the book. Part II treats the broad subject of health risk assessment (HRA), including such topics as health problem identification, toxicology, exposure assessment, and health risk characterization. The chapters in Part III provide material related to hazard risk assessment (HZRA), including topics such as probability calculations, consequence estimation, and hazard risk characterization. Part IV examines risk assessment from a case study perspective; chapters in this final part include material on four subject areas that includes applications and calculations for risk assessments of real systems.

Part I of this book serves as an introduction to the general subject of *Health risk and hazard risk*. There are six chapters in Part I. An introduction to the subject is presented in Chapter 1, along with definitions, risk terms, and financial risk topics. Chapters 2 and 3 examine health problems and hazard problems, respectively, while Chapter 4 discusses the differences between the two. Chapter 5 is concerned with legislation. The major applicable pieces of legislation—the Clean Air Act, the Clean Water Act, the Resource Conservation and Recovery Act (RCRA), the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA), and the Superfund Amendments and Reauthorization Act (SARA)—are discussed. Increased public awareness is the major thrust of the Title III legislation, which is the heart of SARA. SARA Title III established requirements for emergency planning and “community right to know” for federal, state, and local governments as well as for industry, and this topic receives treatment in Chapter 6.

1.4 Definitions

This section defines many of the terms that the reader will encounter in this book. The following list is therefore not a complete glossary of all terms that appear in the risk and risk-related fields. It should also be noted that many of the terms have come to mean different things to different people; this will become evident as one delves deeper into the literature [1].

Acute (risk). Risks associated with short periods of time. For health risk, it usually represents short exposures to high concentrations of a hazardous agent.

Atmospheric dispersion. The mixing of a gas or vapor (usually from a discharge point) with air in the lower atmosphere. The mixing is the result of convective motion and turbulent eddies.

Atmospheric stability. A measure of the degree of atmospheric turbulence, often defined in terms of the vertical temperature gradient in the lower atmosphere.

Auto-ignition temperature. The lowest temperature at which a flammable gas in air will ignite without an ignition source.

Average rate of death (ROD). The average number of fatalities that can be expected per unit time (usually on an annual basis) from all possible risks and/or incidents.

Basic event. A fault tree event (FTE) that is sufficiently basic that no further explanation or development of additional events is necessary.

C (ceiling). The term used to describe the maximum allowable exposure concentration of a hazardous agent related to industrial exposures to hazardous vapors.

Cancer. A tumor formed by mutated cells.

Carcinogen. A cancer-causing chemical.

CAS. Chemical Abstract Service; CAS numbers are used to identify chemicals and mixtures of chemicals.

Catastrophe. A major loss in terms of death, injuries, and damage.

Cause–consequence. A method for determining the possible consequences or outcomes arising from a logical combination of input events or conditions that determine a cause.

Chronic (risk). Risks associated with long-term chemical exposure duration, usually at low concentrations.

Conditional probability. The probability of occurrence of an event given that a precursor event has occurred.

Confidence interval. A range of values of a variable with a specific probability that the true value of the variable lies within this range. The conventional confidence interval probability is the 95% confidence interval, defining the range of a variable in which its true value falls with 95% confidence.

Confidence limits. The upper and lower range of values of a variable defining its specific confidence interval.

Consequences. A measure of the expected effects of an incident outcome or cause.

Continuous release. Emissions that are of an extended or continuous duration.

CPQRA. The acronym for chemical process quantitative risk analysis. It is analogous to a hazard risk assessment (HZRA).

Deflagration. The chemical reaction of a substance in which the reaction front advances into the unreacted substance present at less than sonic velocity.

Delphi method. A polling of experts that involves the following:

1. Select a group of experts (usually three or more).
2. Solicit, in isolation, their independent estimates of the value of a particular parameter and their reason for the choice.
3. Provide initial analysis results to all experts and allow them to then revise their initial values.
4. Use the average of the final estimates as the best estimate of the parameter. Use the standard deviation of the estimates as a measure of uncertainty.

The procedure is iterative, with feedback between iterations. One of the authors modestly refers to it as the Theodore method.

Dermal. Applied to the skin.

Detonation. A release of energy caused by a rapid chemical reaction of a substance in which the reaction front advances into the unreacted substance present at greater than sonic velocity.

Dike. An embankment that restricts the movement of liquid.

Dispersion coefficient. The standard deviation, σ , in a specified direction used in a Gaussian plume atmospheric dispersion model.

Domino effects. The triggering of secondary events; usually considered when a significant escalation of the original incident could result.

Dose. A weight (or volume) of a chemical agent, usually normalized to a unit of body weight.

Episodic release. A massive release of limited or short duration, usually associated with an accident.

Equipment reliability. The probability that, when operating under stated conditions, the equipment will perform its intended purpose for a specified period of time.

Ergonomics. The interaction between humans and their environment, usually in an industrial or other man-made setting.

Event. An occurrence associated with an incident either as the cause or a contributing cause of the incident, or as a response to an initiating event.

Event sequence. A specific sequence of events composed of initiating events and intermediate events that may lead to a problem or an incident.

Event tree analysis (ETA). A graphical logic model that identifies and attempts to quantify possible outcomes following an initiating event.

Explosion. A release of energy that causes a pressure discontinuity or blast wave.

Exposure period. The duration of an exposure.

External event. A natural or man-made event; often an accident.

Failure frequency. The frequency (relative to time) of failure.

Failure mode. A symptom, condition, or manner in which a failure occurs.

Failure probability. The probability that failure will occur, usually in a given time interval.

Failure rate. The number of failures divided by the total elapsed time during which these failures occur.

Fatal accident rate (FAR). The estimated number of fatalities per 10^8 exposure hours (roughly 1000 employee working lifetimes).

Fault tree. A method for representing the logical combinations of events that lead to a particular outcome (top event).

Fault tree analysis (FTA). A logic model that identifies and attempts to quantify possible causes of an event.

Federal Register. A daily government publication of laws and regulations promulgated by the U.S. Federal Government.

Flammability limits. The range in which a gaseous compound in air will explode or burst into flames if ignited.

Frequency. Number of occurrences of an event per unit time.

Gaussian model. A plume dispersion model based on mixing and turbulence in the lower atmosphere.

Half-life. The time required for a chemical concentration or quantity to decrease by half its current value.

Hazard (problem). An event associated with an accident, which has the potential for causing damage to people, property, or the environment.

Hazard and operability study (HAZOP). A technique to identify process hazards and potential operating problems using a series of guide words that key on process deviations.

Hazard risk assessment (HZRA). A technique associated with quantifying the risk of a hazard employing probability and consequence information.

Health (problem). A problem normally associated with and arising from the continuous emission of a chemical into the environment.

Health risk assessment (HRA). A technique associated with quantifying the risk of a health problem employing toxicology and exposure information.

Human error. Actions by engineers, operators, managers, etc., that may contribute to or result in accidents.

Human error probability. The ratio between the number of human errors and the number of opportunities for human error.

Human factors. Factors attempting to match human capacities and limitations.

Human reliability. A measure of human errors.

Incident. An event.

Individual risk. The risk to an individual.

Ingestion. The intake of a chemical through the mouth.

Initiating event. The first event in an event sequence.

Instantaneous release. Emissions that occur over a very short duration.

Intermediate event. An event that propagates or mitigates the initiating event during an event sequence.

Isopleth. A concentration plot at specific locations, usually downwind from a release source.

Lethal concentration (LC). The concentration of a chemical that will kill a test animal, usually based on 1–4 h exposure duration.

Lethal concentration 50 (LC₅₀). The concentration of a chemical that will kill 50% of test animals, usually based on 1–4 h exposure duration.

Lethal dose (LD). The quantity of a chemical that will kill a test animal, usually normalized to a unit of body weight.

Lethal dose 50 (LD₅₀). The quantity of a chemical that will kill 50% of test animals, usually normalized to a unit of body weight.

LEL/LFL. The lower explosive/flammability limit of a chemical in air that will produce an explosion or flame if ignited.

Level of concern (LOC). The concentration of a chemical above which there may be adverse human health effects.

Likelihood. A measure of the expected probability or frequency of occurrence of an event.

Logic gate. A symbol in a logic diagram that specifies the logical combination of inputs required for an output to be propagated.

Malignant. A cancerous tumor.

Mutagen. A chemical capable of changing a living cell.

PEL. The permissible exposure limit of a chemical in air, established by the Occupational Safety and Health Administration (OSHA).

Personal protection equipment (PPE). Material/equipment worn to protect a worker from exposure to hazardous agents.

Precision. The degree of “exactness” of repeated measurements.

ppm. The parts per million of a chemical in air—almost always on a volume basis; often designated as ppmv as opposed to ppmm (mass basis).

ppb. The parts per billion of a chemical in air—almost always on a volume basis; often designated as ppbv as opposed to ppbm (mass basis).

Maximum individual risk. The highest individual risk in an exposed population.

Probability. An expression for the likelihood of occurrence of an event or an event sequence, usually over an interval of time.

Propagating factors. Influences that contribute to the sequence of events following the initiating event.

Protective system. Systems, such as pressure vessel relief valves, that function to prevent or mitigate the occurrence of an accident or incident.

Risk. A measure of economic loss or human injury in terms of both the incident likelihood and the magnitude of the loss or injury.

Risk analysis. The engineering evaluation of incident consequences, frequencies, and risk assessment results.

Risk assessment. The process by which risk estimates are made.

Risk contour. Lines on a risk graph that connect points of equal risk.

Risk estimation. Combining the estimated consequences and likelihood of a risk.

Risk management. The application of management policies, procedures, and practices in analyzing, assessing, and controlling risk.

Risk perception. The perception of risk that is a function of age, race, sex, personal history and background, familiarity with the potential risk, dread factors, perceived benefits of the risk causing action, marital status, residence, etc.

Societal risk. A measure of risk to a group of individuals.

Source term. The estimation of the release of a hazardous agent from a source.

Time of failure. The time period associated with the inability to perform a duty or intended function.

TLV. The threshold limit value (established by the American Council of Government Industrial Hygienist). The concentration of a chemical in air that produces no adverse effects.

TLV-TWA. The allowable time weighted average concentration of a chemical in air for an 8 h workday/40 h workweek that produces no adverse effect.

TLV-STEL. The short-term exposure limit (maximum concentration in air) for a continuous 15 min averaged exposure duration.

TLV-C. The ceiling exposure limit representing the maximum concentration of a chemical in air that should never be exceeded.

Top event. The accident, event, or incident at the “top” of a fault tree that is traced downward to more basic failures using logic gates to determine their causes.

Toxic dose. The combination of concentration and exposure period for a toxic agent to produce a specific harmful effect.

UEL/UFL. The upper explosive/flammability limit of a chemical in air that will produce an explosion or flame if ignited.

Uncertainty. A measure, often quantitative, of the degree of doubt or lack of certainty associated with an estimate.

Finally, the reader should carefully note the difference between the definitions of *health* and *hazard*.

Illustrative Example 1.1

Define hazard [2].

Solution

Hazard, risk, failure, and reliability are interrelated concepts concerned with uncertain events and therefore amenable to quantitative measurement via probability. *Hazard* is generally defined as a potentially dangerous event, for example, the release of toxic fumes, a power outage, or

pump failure. The potential danger represented by a hazard results in undesirable consequences associated with risk. The reader may choose to compare this with the definition provided in Section 1.4.

Illustrative Example 1.2

Define risk [2].

Solution

Risk is defined as the product of two factors: (1) the probability of an undesirable event, and (2) the measured consequences of the undesirable event. Measured consequences may be stated in terms of financial loss, injuries, deaths, or other variables.

Illustrative Example 1.3

Define failure.

Solution

Failure represents an inability to perform some required function. The reader may choose to compare this to the definition found in Section 1.4.

Illustrative Example 1.4

Define reliability.

Solution

Reliability is the probability that a system or one of its components will perform its intended function under certain conditions for a specified period. The reliability of a system and its probability of failure are complementary in the sense that the sum of these two probabilities is unity. The basic concepts and theorems of probability that find application in the estimation of risk and reliability are considered in Chapter 14.

1.5 Risk Terms

Is risk important to the practitioner? The reader can decide since all actions, objects, processes, etc., have risk. Add to this the risk associated with gambling. It is no wonder that this four letter word has become a hot ticket for practitioners.

Section 1.4 contained a host of terms and their accompanying definitions. Several of the terms contained with word *risk*. The so-called traditional definitions associated with these words or phrases were presented at that time. This section attempts to review not only the myriad of risk and risk-related

terms but also some of the myriad of accompanying definitions that have been used in industry and have appeared in the literature. No attempt has been made to present this list in alphabetical order. Rather this approach has attempted to provide the various terms in a logical, sequential order.

The four major risk terms include

- Risk
- Risk assessment
- Risk analysis
- Risk management

Risk was defined earlier as a measure of economic loss, human injury, or human health effect, and in terms of both the likelihood (probability) and the magnitude (consequences) associated with either a loss or injury. Although it is a quantifiable term, it has been misused by practitioners. *Risk assessment* involves the process of determining the events or problems that can produce a risk, the corresponding probabilities and consequences, and finally, the characterization of the risk. *Risk analysis* employs the results of the aforementioned risk assessment and attempts to optimally use these results; in effect, it analyzes risk assessment information. Finally, *risk management* uses all the information provided by the risk assessment and risk analysis steps to reduce or eliminate the risk, select the optimum action(s), or evaluate the net benefits versus health/safety concerns. Note, however, that in line with the title, this book is primarily concerned with risk assessment calculations from both a health and hazard perspective.

Of course, there are other risks. The definitions (for purposes of this section) for these other risks follow: *Individual risk* is defined as the risk to an individual; this can include a health problem or injury, the likelihood of occurrence, and the time period over which the problem might occur. The *maximum individual risk* is the aforementioned individual risk to a person exposed to the highest risk in an exposed population; this can be determined by calculating individual risks at every “location” and selecting the result for the maximum value. The *average individual risk* (in an *exposed* population) is the aforementioned individual risk averaged over the total population that is exposed to the risk in question. Alternatively, the *average individual risk* (in a *total* population) is the individual risk averaged over the entire population without regard to whether or not all the individuals in the population are actually exposed to the risk. Unfortunately, this particular average risk—whether applied to employees or the public—can be (at times) extremely misleading. These average risks have, on occasion, been expressed as exposed hours per worked hours; thus, the risk may be calculated for a given duration of time or averaged over the working day. *Societal risk* provides a measure of risk to specific groups of people, i.e., it is based on the people affected by an event/scenario. (See also Chapter 21, Case Study 1, for the application of several of these risk terms to an industrial accident).

Time to respond risk characterizes the time that a response occurs following a given event/scenario. *Risk communication* is concerned with communicating the information generated from a risk assessment, risk analyses, and a risk management study. *Ecological risk* is a risk that describes the likelihood that adverse ecological effects resulting from an event/scenario will occur. *Total risk* is the term generally employed to describe the summation of the risk from all events/scenarios. *De minimus risk* recently has taken on significant importance, in toxicology (see Chapter 9). It is defined as a risk judged to be too insignificant to be of societal concern or too small to be effectively applied to standard risk assessment studies. *Financial risk* is important enough to receive treatment in a separate section that follows.

Risk terms will be revisited in Chapter 4. However, it should be noted that from a regulatory point of view, EPA has provided information on how risk is used to develop regulations. This was presented as part of a preamble to a proposed regulation for halogenated solvent cleaning that was published in October 2008 and that can be found at the following URL: <http://www.epa.gov/ttn/atw/degree/fr20oc08.pdf>

Illustrative Example 1.5

Define health risk characterization.

Solution

In health risk characterization, toxicology and exposure data/information are combined to obtain a qualitative or quantitative expression of risk. See Part II for extensive details on this topic.

Illustrative Example 1.6

Define comparative risk assessment.

Solution

Comparative risk assessment is the comparison of potential risks associated with a variety of activities and situations so that a specific action can be placed in perspective relative to other risks. An attempt is often made to compare an individual's risk of death or cancer from exposure to a hazardous waste site with that associated with traveling in an automobile or eating a peanut butter sandwich. Both of these latter events have relatively high risks but are perceived by the public to have a relatively low risk when compared to the risk of a hazardous waste site.

Illustrative Example 1.7

Compare annual versus lifetime risks.

Solution

A time frame must be included with a risk estimate for the numbers to be meaningful. For both health and hazard risks, annual or lifetime

risks are commonly used. Direct evidence is usually expressed annually because the information is often collected and summarized annually. However, predictive information is commonly expressed as a lifetime probability, e.g., when expressing cancer risk or a terrorist-related risk.

Illustrative Example 1.8

Define an accident.

Solution

As noted earlier, an accident is an unexpected event that has undesirable consequences and can be quantitatively described through a HZRA. The causes of accidents have to be identified in order to help prevent accidents from occurring. Any situation or characteristic of a system, plant, or process that has the potential to cause damage to life, property, or the environment is considered a hazard. A hazard can also be defined as any characteristic that has the potential to cause an accident.

Illustrative Example 1.9

Describe what a cancer risk number of 10^{-6} probability means.

Solution

A cancer risk number usually represents the probability of developing cancer risk. A risk of 10^{-6} indicates an individual has a 1 in 1,000,000 chance of developing cancer throughout a lifetime (assumed to be 70 years). One generally can also assume an upper 95% confidence limit on the maximum likelihood estimate. Since the predicted risk is an upper bound, the actual risk is unlikely to be higher but may be much lower than the predicted risk.

1.6 Financial Risk

As noted previously, there are other risks—in addition to environmental ones [3]—that the practicing engineer and applied scientist must be proficient in understanding. Perhaps the most important of these is financial risk. And, although this chapter is primarily concerned with health risk and hazard risk, the authors would be negligent if the topic of financial risk were not at least qualitatively addressed.

A company or individual hoping to increase profitability must carefully assess a range of investment opportunities and risks and select the most profitable options from those available. Increasing competitiveness also requires that efforts need to be made to reduce the costs of existing processes. In order

to accomplish this, engineers and scientists should be fully aware of not only technical factors but also economic factors, particularly those that have the largest effect on financial risk and the accompanying topic of profitability.

In earlier years, engineers and scientists concentrated on the technical side of projects and left the financial studies to the economist. In effect, those involved in making estimates of the capital and operating costs have often left the overall economic analysis and investment decision making to others. This approach is no longer acceptable.

Some technical personnel are not equipped to perform a financial and/or economic analysis. Furthermore, many already working for companies have never taken courses in this area. This short-sighted attitude is surprising in a group of people who normally go to great lengths to obtain all the available technical data they can before making an assessment of a project or study. The attitude is even more surprising when one notes that data are readily available to enable an engineer or scientist to assess the prospects of both his or her own company and those of his or her particular industry [4].

The term *economic analysis* in real-world problems generally refers to calculations made to determine the conditions for realizing maximum financial return for a design or operation. The same general principles apply whether one is interested in the choice of alternatives for completing projects, in the design of plants so that the various components are economically proportioned, or in the economical operation of existing plants. General considerations that form the framework on which sound decisions must be made are often simple. Sometimes their application to the problems encountered in the development of a commercial enterprise involves too many intangibles to allow exact analysis; in that case, judgment must be intuitive. Occasionally, such calculations may be made with a considerable degree of exactness.

Concern with maximum financial return implies that the criterion for judging projects involved is risk and profit. While this is usually true, there are many important objectives, which, though ultimately aimed at increasing profit, cannot be immediately evaluated in quantitative terms. Perhaps the most significant of these is the recent increased concern with environmental degradation, safety, and sustainability. Thus, there has been some tendency in recent years to regard management of commercial organizations as a profession with social obligations and responsibilities; considerations other than the profit motive may govern business decisions. However, these additional social objectives are, for the most part, often not inconsistent with the economic goal of satisfying human wants with the minimum risk. In fact, even in the operation of primarily nonprofit organizations, it is still important to determine the effect of various policies on both risk and long-term economic viability [5].

If all industrial financial studies simply involved running costs, where a day-to-day expenditure of appropriate raw materials and labor would produce a product of immediate market value, risk predictions as to the future demand and prices would be minimized. However, any future return over a period of time can best be evaluated by a host of different methods.

In order to accomplish this, appropriate data for the value of money, i (*interest rate*), and the lifetime, n , of the process are needed. To a certain extent, the values chosen are interdependent. A large n and a small i can give the same result as a small n and a large i . The result is often evaluated in terms of a lump sum expressed as a present worth factor.

First, financial risks are not governed purely by chance like the role of the dice. What appears as a sound investment to engineers, scientists, and business executives, familiar with the know-how and experience in a given company, might represent a highly speculative venture for a concern engaged largely in a different type of business. Similarly, one investor in common stock of a given company may not agree with another who does not see growth possibilities in the same stock. Thus, the situation exists that some ventures (investments) require a higher rate of return than others simply because such a rate is necessary to attract venture capital.

Second, aside from the chance of success or failure, a given company is limited in the amount of funds it can invest either from surplus or by borrowing. Thus, in offshore crude oil exploration, a large company (such as British Petroleum) that can finance the drilling of a number of oil wells can recover the costs of unsuccessful ventures from the profits of successful ones and, on the average, show attractive returns, even though four out of five wells drilled turn out to be “dry” holes. The position of the wildcatter or small operator is different in that an unlucky run of failures can put him/her out of business. Companies, like individuals, are limited in the absolute amount of capital they can afford to invest, and, as proposed ventures approach this limit, the rate of return required will increase, even though the financial risk remains unchanged. The utility of a large gain must therefore be balanced against the disutility of a smaller loss, which may mean disaster.

In modern business, which is often run by corporations, the entrepreneur is, for the most part, the common stockholder. It is true that the actual operations of the company are in the hands of business executives, and their salaries depend in large part on their ability to show profits. Often, however, their fortunes may not be intimately linked with those of the companies they manage if they own only modest amounts of stock in their concerns. Furthermore, their salaries, as reported in the media in recent years—though astronomically high—do not represent a major expense in company operations. If the company they represent fails, they are often able to find opportunities for employment elsewhere. Similarly, the bondholder and preferred stockholder are protected to varying degrees from the risk of company failure. The holder of common stock, on the other hand, is subject to all the risks inherent in running the business. A proper procedure for evaluating new-venture capital risk should, therefore, take these factors into consideration.

Financial risk inevitably comes into play in any risk management study. And, no discussion of financial risk would be complete without an introduction to the net present value (NPV). Most monetary dealings involve

expenditures and revenues, both of which usually occur at different times. NPV allows the practitioner to effectively record and compare the costs (C) and revenues (R) as demonstrated in Equation 1.1:

$$\text{NPV} = (R_0 - C_0) + \frac{(R_1 - C_1)}{(1+i)} + \frac{R_2 - C_2}{(1+i)^2} + \dots \quad (1.1)$$

The subscripts refer to a time period that normally represents years, while i refers to the discount rate (approximately equal to the value of money, i.e., the interest rate) for the time period in question. The higher the NPV, the more attractive is the monetary dealing or project. Thus, this simple equation allows one to compare a series of costs and revenues. When applied to projects/dealings/activities concerned with risk, the terms R and C would represent, in a general sense, the benefits associated with the costs of reducing/eliminating the risks [3–6].

Illustrative Example 1.10

List the major *fixed* capital costs for the chemical process industry.

Solution

1. Major process equipment (i.e., reactors, tanks, pumps, filters, distillation columns, etc.)
2. Installation of major process equipment
3. Process piping
4. Insulation
5. Instrumentation
6. Auxiliary facilities (i.e., power substations, transformers, boiler houses, fire-control equipment, etc.)
7. Outside lines (i.e., piping external to buildings, supports and posts for overhead piping, electric feeders from power substations, etc.)
8. Land and site improvements
9. Buildings and structures
10. Consultant fees
11. Engineering and construction (design and engineering fees plus supervision of plant erection)
12. Contractors' fees (administrative)

Illustrative Example 1.11

List the major *working* capital costs for the chemical process industry.

Solution

1. Raw materials for plant startup
2. Raw material, intermediate and finished product inventories

3. Cost of handling and transportation of materials to and from sites
4. Cost of inventory control, warehouse, associated insurance, security arrangements, etc.
5. Money to carry accounts receivable (i.e., credit extended to customers) less accounts payable (i.e., credit extended by suppliers)
6. Money to meet payrolls when starting up
7. Readily available cash for emergencies
8. Any additional cash required to operate the process or business
9. Expenses associated with new hires
10. Startup consultant fees

Illustrative Example 1.12

A process emits 50,000 acfm of toxic gas containing a dust (it may be considered a metal) at a loading of 2.0 g/ft³. A particulate control device is employed not only for particle capture but also because the metal captured from the unit is worth \$0.03/lb of particulate. Experimental data have shown that the particle collection efficiency, E , is related to the system pressure drop, ΔP , by the formula:

$$E = \frac{\Delta P}{\Delta P + 15.0} \quad (1.2)$$

where

E is the *fractional* collection efficiency

ΔP is the pressure drop, lb_f/ft²

If the fan is 55% efficient (overall) and electric power costs \$0.18/kW-h, at what collection efficiency is the cost of power (CP) equal to the value of the recovered metal? What is the pressure drop in inches of water (in H₂O) at this condition?

Solution

The value of the recovered material (RV) may be expressed in terms of the fractional collection efficiency, E , the volumetric flow rate, q , the inlet metal loading, c , and the value of the dust, DV :

$$RV = (q)(c)(DV)(E) \quad (1.3)$$

Substituting yields

$$\begin{aligned} RV &= \left(\frac{50,000 \text{ ft}^3}{\text{min}} \right) \left(\frac{2.0 \text{ g}}{\text{ft}^3} \right) \left(\frac{1 \text{ lb}}{7,000 \text{ g}} \right) \\ &\times \left(\frac{\$0.03}{\text{lb}} \right) (E) = \$0.429E/\text{min} \end{aligned}$$

The recovered value can be expressed in terms of pressure drop, i.e., replace E by ΔP :

$$RV = \frac{(0.429)(\Delta P)}{\Delta P + 15.0} \$/\text{min} \quad (1.4)$$

The CP in terms of ΔP , q , the cost of electricity (CE), and the fan fractional efficiency, E_f is

$$CP = \frac{(q)(\Delta P)(CE)}{(E_f)} \quad (1.5)$$

Substitution yields

$$\begin{aligned} CP &= \left(\frac{50,000 \text{ ft}^3}{\text{min}} \right) \left(\frac{\Delta P \text{ lb}_f}{\text{ft}^2} \right) \left(\frac{\$0.18}{\text{kW-h}} \right) \left(\frac{1 \text{ min-kW}}{44,200 \text{ ft-lb}_f} \right) \\ &\times \left(\frac{1}{0.55} \right) \left(\frac{1 \text{ h}}{60 \text{ min}} \right) = 0.006 \Delta P \$/\text{min} \end{aligned}$$

The pressure drop at which the cost of power is equal to the value of the recovered metal is found by equating RV to CP :

$$RV = CP \quad (1.6)$$

Solving the resulting equation yields

$$\square P = 66.5 \text{ lb}_f/\text{ft}^2 = 128 \text{ in H}_2\text{O}$$

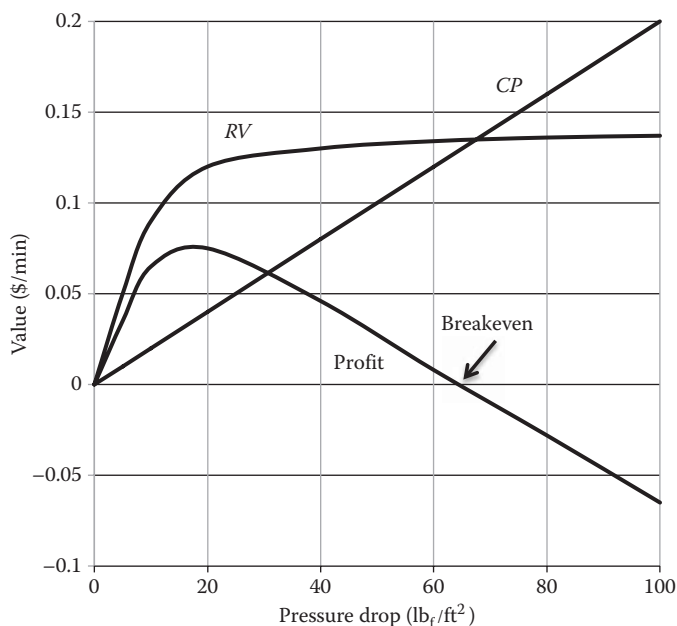
Figure 1.1 shows the variation of RV , CP , and profit as a function of pressure drop across the system.

The collection efficiency corresponding to the ΔP calculated previously is

$$E = \frac{\Delta P}{\Delta P + 15.0} = \frac{66.5 \text{ lb}_f/\text{ft}^2}{66.5 \text{ lb}_f/\text{ft}^2 + 15.0} = 0.82 = 82\%$$

The reader should note that operating below this efficiency (or the corresponding pressure drop) will produce a profit; operating above this value leads to a loss.

The operating condition for maximum profit can be estimated from Figure 1.1. Calculating this value is left as an exercise for the reader. (*Hint*: Set the first derivative of the profit [i.e., $RV - CP$] with respect to ΔP equal to zero. The answer is $13.9 \text{ lb}_f/\text{ft}^2$.)

**FIGURE 1.1**

Profit as a function of pressure drop.

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2

History of Environmental Health Problems

2.1 Introduction

BANG! The Big Bang. In 1948, physicist G. Gamow proposed the Big Bang Theory of the origin of the universe. He believed that the universe was created in a gigantic explosion as all mass and energy were created in an instant of time. Estimates on the age of the universe at the present time range between 7 and 20 billion years, with 13.5 billion years often mentioned as the age of the planet Earth [1].

The bang occurred in a split second and within a minute the universe was approximately a trillion miles wide and expanding at an unbelievable rate. Several minutes later, all the matter known to humanity had been produced. The universe as it is known today was in place [1].

Gamow further believed that the various elements observed today were produced within the first few minutes after the Big Bang, when near infinitely high temperatures fused subatomic particles into the chemical elements that now comprise the universe. More recent studies suggest that hydrogen and helium would have been the primary products of the Big Bang, with heavier elements being produced later within the stars. The extremely high density within the primeval atom caused the universe to expand rapidly. As it expanded, the hydrogen and helium cooled and condensed into stars and galaxies. This perhaps explains the expansion of the universe and the physical basis of Earth [1].

Over the course of history, people who learned from health and health-related problems survived to learn again and reproduced, while those who did not disappeared. Environmental concerns took hold at about 3000 B.C. Urban areas on the Indian continent developed sanitation programs such as underground drains and public baths. Aspects of health were integrated with daily activities, including personal hygiene, health education, exercise, dietary practices, food and environmental sanitation, plus treatment of minor accidents and injuries. By 1400 B.C., this early society featured total health care through health promotion and education, along with advances in curative medicine and surgery. These methods were also developed in ancient Greece and Rome.

Regarding industrial hygiene, Hippocrates noted the toxicity associated with lead in the mining industry in 400 B.C. The Greek physician Galen noted, in 200 A.D., the health effects suffered by copper miners from acid mist exposure. Several books had an impact on their occupational health science, including

1. Agricola's *De Re Metallica* (*On the Nature of Metals*)
2. Ramazzini's *De Morbis Antificum Diatriba* (*The Disease of Workmen*)
3. Ellensburg's publication on gold miner injuries, occupational deceases, and the toxicity of mercury, lead, and carbon monoxide

Regarding risk, the formed concepts of risk and quantifying such can be traced back to the sixteenth or seventeenth century when it was discovered that probability theory could be used to estimate the odds (a probability component of risk) in games of chance in gambling. This capability lead to the development of a new business—insurance—that now depends on its ability to predict and quantify risks.

One of the significant documents published in 1976 by the EPA was the *Guidelines for Carcinogenic Risk Assessment*. This document stated that carcinogenic risk assessment should include the following

1. Determine whether a particular substance constitutes a cancer risk
2. Determine what regulatory action, if any, should be taken to reduce that risk
3. Conduct analyses of health risks independently from considerations of the socioeconomic consequence of the regulatory action
4. Provide a judgment concerning the weight of evidence that an agent or chemical is a potential human carcinogen
5. Determine how great an impact a chemical exposure is likely to have on public health
6. Regard risk estimates only as rough indications of potential effects
7. Involve calculations using a variety of risk extrapolation methods
8. Clearly define the uncertainty in the data and extrapolation methods employed
9. Summarize the known and possible exposure modes associated with the various uses of the chemical

Much of the aforementioned was overshadowed in the previous century by the great advances in the prevention and treatment of disease. The past two decades has produced a resurgence of interest in proactive health protection and risk reduction.

Flash forward to the present. More than any other time in history, this century will be a turning point for human civilization. Human beings may be

facing ecological disasters that could affect their ability to survive. These crises could force society to reexamine the value system that has governed lives for the past 2 million years of existence [2]. At some point during its earlier journey, much of human society lost its feeling of connectedness to nature, resulting in a “we can manage the world” attitude. This attitude might ultimately lead to the destruction of this country and the world.

The big question now asked is: How did it come to this? The answer lies in a knowledge of human history, a surprisingly brief chapter in the chronicle of the planet—how brief can be demonstrated by the use of a standard calendar to mark the passage of time on Earth. The origin of the Earth, estimated to be some several billion years ago, is placed at midnight January 1, 2011, and the present at midnight December 31, 2011. Each calendar day represents approximately 12 million years of actual history. Using this time scheme, dinosaurs arrived about December 10 and disappeared on Christmas day. The first humans can be placed at 11:45 PM on December 31. The recorded history of human achievement takes up only the last minutes of the world’s existence in this scheme [2].

The remainder of this chapter describes the path that led to this dangerous predicament. However, this path is now leading a growing number of individuals to unite in a broad social movement called environmentalism: a movement that some claim is charting a path out of this predicament. The following topics are addressed in this chapter:

- First humans
- Developments of agriculture
- Colonization of the new world
- Industrial revolution

2.2 First Humans

Environmental problems have bedeviled humanity since the first person discovered fire. The earliest humans appear to have inhabited a variety of locales within a tropical and semitropical belt stretching from Ethiopia to southern Africa about 1.9 million years ago. These first humans provided for themselves by a combination of gathering food and hunting animals. Humans, for the majority of their 2 million years’ existence, lived in this manner. The steady development and dispersion of these early humans was largely due to an increase in their brain size. This led to an ability to think abstractly, which was vital in the development of technology and advanced communication. This, in turn, led to cooperation and more elaborate social organization [3]. The ability to use and communicate the developed technology to others to

overcome hostile environments ultimately led to the expansion of these first human settlements.

With the use of primitive tools and skins of animals for clothes, the first humans moved outside Africa about one and a half million years ago. The migration led them into the frost-free zones of the Middle East, India, southern China, and parts of Indonesia. Humans at this time could only adapt to those ecosystems found in the semitropical areas that contained a wide variety of vegetation and small, easily hunted animals to supplement their diet. Despite relatively easy access, Europe was not settled for a long period of time due to the deficient ecosystem, which was later overcome by an increase in technology. The first evidence of human settlement in Europe is estimated to have occurred approximately 730,000 years ago. The settlement of America was almost the last stage in the movement of humans across the globe about 20,000 years ago. This was made possible by crossing to Alaska in the last glaciation when reduced sea levels turned the Bering Strait into a land bridge. Once the first human settlers were able to move south through the passes, they found an enormously rich environment that supplied abundant food. The human population multiplied rapidly and within a few thousand years had spread to the tip of South America.

Approximately 10,000 years ago humans had spread over every continent, living in small mobile groups. A minority of these groups lived in close harmony with the environment and did minimal damage. Evidence has been found where groups tried to conserve resources in an attempt to maintain subsistence for long periods of time. In some cases, restrictions on hunting a particular species at a certain time of the year or only in a certain area every few years helped to maintain population levels of certain animals [4]. The Cree in Canada used a form of rotational hunting, only returning to an area after a considerable length of time, which allowed animal populations to recover. But the majority of these groups exploited the environment and the animals inhabiting it. In Colorado, bison were often hunted by stampeding them off a cliff, ending up with about 200 corpses, most of which could not be used. On Hawaii, within a thousand years of human settlement, 39 species of land birds had become extinct [3]. Over the last 100,000 years, 86% of the large animals in Australia have become extinct. The large numbers of species lost was largely due to the tendency for hunters to concentrate on one species to the exclusion of others. The main reason why these groups avoided further damage to nature was the fact that their numbers were so small that the pressure they exerted on the environment was minimal.

2.3 Development of Agriculture

Major changes began to take place between 10,000 and 12,000 years ago. Humans learned how to domesticate animals and cultivate plants and, in

doing so, made a transition from nomadic hunter gatherer to rooted agriculturalist. The global population at this time was about 4 million people, which was about the maximum that could readily be supported by a gathering and hunting way of life [3]. The increasing difficulty in obtaining food is believed to be a primary contributor to this sudden change to agrarian societies. The farmer changed the landscape of the planet and was far more destructive than the hunter. While farming fostered the rise of cities and civilizations, it also led to practices that denuded the land of its nutrients and water-holding capacity. Great civilizations flourished and then disappeared as once-fertile land, after generations of over-farming and erosion, was transformed into barren wasteland.

The adoption of agriculture, combined with its two major consequences (settled communities and a steady rise in population), placed an increasing strain on the environment. The strain was localized at first but as agriculture spread so did its effects. Agriculture involved replacing the natural habitat with an artificial habitat where humans could grow the plants and stock the animals they needed. The natural balance and inherent stability of the original ecosystem were thereby destroyed. Instead of a variety of plants and permanent natural ground cover, a small number of crops made only part-time use of the space available. The soil was exposed to wind and rain to a far greater extent than before, particularly where fields were left barren for part of the year, thus leading to a higher rate of soil erosion than under natural ecosystem conditions. Nutrient recycling processes were also disrupted and additional inputs in the form of manures and fertilizers were therefore required if soil fertility was to be maintained. The adoption of irrigation was even more disruptive since it created an environment that was even more artificial. Adding large amounts of water to a poor soil would allow farmers to grow preferred crops, but it would prove to have catastrophic long-term effects. The extra water would drain into the underlying water table, sometimes leading to rising water levels that caused the soil to become waterlogged. This additional water not only altered the mineral content of the soil but also increased the amount of salt and eventually—especially in arid areas with high evaporation rates—produced a thick layer of salt on the surface that made agriculture impossible. In addition, the emergence of villages and towns meant that the demand for resources was now more concentrated.

These early societies were dependent on the production of a food surplus in order to feed and support the growing number of priests, rulers, bureaucrats, soldiers, craftsmen, and ordinary people. Forests suffered the most as the demand grew for wood to build houses, heat homes, and cook. Local deforestation around settled areas added to the increase of soil erosion. Soil erosion then led to badly damaged landscapes, declining crop yields and eventually an inability to grow a surplus of food. The first signs of widespread damage emerged in Mesopotamia, the area where the most extensive modifications to the natural environment were first made.

Both domestication of animals and the cultivation of plants had dramatic impacts on the environment. The nomadic hunters and gatherers were aware that they shared the earth with other living things. Animals and humans were able to live in the same area since the hunters and gatherers did not destroy the ecosystem to a great extent. The agriculturalist, on the other hand, deliberately transformed nature in an attempt to simplify the world's ecosystem. As an example, by plowing and seeding a grassland, a farmer would eliminate a hundred species of native herbs and grasses, which would then be replaced with pure strands of wheat, corn, or alfalfa. This simplification reduced the stability of the ecosystem, making it uninhabitable for most animals.

2.4 Colonization of the New World

Only slightly more than 500 years, a mere second on the geological clock has passed since Columbus' discovery opened a new world to the Europeans: a land with few indications of human occupation except for a few thin plumes of smoke rising from cooking fires in small clearings in the woods. These clearings belonged to the Native Americans, which numbered about 4 million at this time. Over the centuries, these native peoples had created their own complex culture. Their means of sustaining themselves did not rely on scarring or subduing the Earth but on using what it offered. Native American society was not separate from nature, but part of it. Geography, as well as history, began to change when Christopher Columbus anchored his little fleet off the island of San Salvador. Like most of those who followed, Columbus and his company risked the voyage to the New World for what they could take from it. They came for gold, a trade route to the spices of India, and other riches of Asia: land, goods to sell, glory, adventure, religious and personal freedom, and, in some cases, to convert the heathen to Christianity [5]. However, it was what they brought with them, far from what they took, that changed the face of the continent forever. What they brought was Europe's 2000 or more years of western history, customs, prejudices, and methodology. They brought European technology, philosophy, religion, aesthetics, a market economy, and a talent for political organization. They brought European diseases that decimated the native people. They also brought with them European ideas of what the New World was and visions of what it should be.

In the beginning, the explorers and first settlers were faced by a dark forbidding line of forest behind which was a vast, unmapped continent that was inhabited by "savages" and filled with ferocious "wild beasts." Mere survival meant conquering the wilderness. The forest had to be cleared to make way for living space and to provide wood for shelters and fires [6].

Behind the trees lurked the Indians, ready, the settlers suspected, to commit unspeakable atrocities. The forest was filled with wolves, bears, and panthers that they feared would pounce on their children and domestic animals. The greater the destruction of the forest, the greater the safety for the tiny communities clinging to the edge of the hostile continent. Removing the trees also opened land for crops and cattle. Killing the wild animals not only filled the pot with meat but also eliminated the deer and other grazing animals that stole the settlers' corn [6].

The European population quickly grew beyond the carrying capacity of the land. Cropland was frequently exhausted by permanent cultivation; cattle, swine, and sheep introduced by immigrants made far heavier demands on field and forest than wild animals. As each new field was harvested, the chemical, mineral, and biological nature of the soil itself was depleted. The Europeans also brought technology that contributed to the heavy impact they had on the land. Horses and oxen enabled the settlers to open and cultivate vast areas. Plows could dig deeply into the soil, exposing far more loam. With draft animals, the Europeans could harvest heavier loads and transport them to markets. Sailing ships could then transport those loads along the coast or across the ocean.

Whereas the Native Americans would take from the land only what they could consume, the colonist and their successors sought to grow surplus that they could sell for cash or trade for manufactured goods and other commodities. The production of surplus led to the accumulation of capital and the creation of wealth, largely in the towns that served as marketplaces. That meant clearing more land, cutting more timber, planting more crops, and raising more cattle, all at a rate that could be sustained only at a cost of permanent damage to the land. The deforestation of New England and the disappearance of the beaver in the East are but two dramatic examples of how the demands of the market could deplete abundant resources in short order. By the time of the American Revolution, the wilderness along the eastern seaboard had been tamed. While some pockets of forest remained, the 13 colonies were largely covered with farms, dotted with villages, and punctuated by a few substantial cities, notably Boston, New York, Philadelphia, and Charleston.

2.5 Industrial Revolution

Early in the nineteenth century, an awesome new force was gathering strength in Europe. The term "industrial revolution" was coined by the French as a metaphor of the affinity between technology and the great political revolutions of that time. When this was exported to the United States, the industrial revolution swept away any visions of America remaining an

agrarian society. The steam engine, the railroad, the mechanical thresher, and hundreds of other ingenious inventions that increased man's ability to transform the natural world and put it to use would soon be puffing and clattering and roaring in all corners of the land. The new machines swiftly accelerated the consumption of raw materials from the nation's farms, forests, and mines.

Lumbering became the nation's most important industry in the late eighteenth century. Wood was the most widely used raw material for heating, and for building houses, barns, and shops; the same can be said for ships, furniture, railroad ties, factories, and paper making. The supply seemed inexhaustible since the forest still darkened huge parts of the country. Some forests disappeared before the axes of the advancing Americans. The settlers never thought of their axe work as deforestation but as the progress of civilization.

Meanwhile, the big cities and growing wealth of the East were creating a more rapidly expanding market for wheat, corn, beef, and other crops. New roads and canals, the steamboat, and the locomotive made domestic and foreign markets increasingly accessible to farms in the center of the continent. Eli Whitney's cotton gin, Cyrus McCormick's reaper, Benjamin Holt's combine, and other ingenious inventions encouraged the development of a highly productive and efficient agriculture that sharply reduced the biological diversity of the land. Mining both preceded and quickly followed settlement of the interior and left deep and permanent scars on the continent's land and waters. Gold in California, lead in Illinois, coal and oil in Pennsylvania, iron ore in Minnesota, and copper in Montana attracted fortune hunters and job seekers. Reports of a strike would draw thousands of prospectors and workers as well as those who lived off them. Mines were often operated without care for the surrounding countryside. The picks and shovels, the hoses and dredges, and the settlements of the miners created the nation's first widespread pollution and environmental health problems. Mining left behind gutted mountains, dredged-out streams, despoiled vegetation, open pits, polluted creeks, barren hillsides and meadows, a littered landscape, and abandoned camps. Mining contributed to the deforestation of the countryside. Woodlands were often cleared for mining operations; enormous amounts of timber were needed for the posts and beams that supported the mine shafts and fueled smelter operations [5].

Steam shovels came into use in the 1880s, enabling the coal operators of Pennsylvania and the iron ore producers of Minnesota to peel away the very crust of the earth to extract raw materials for industry, creating wealth for themselves in the process. Spoils from the coal started to turn streams more acidic. The discovery of oil in Pennsylvania in 1859 brought drilling rigs that poked into the skyline: large areas of soil were soaked with black ooze [6]. It was in the cities that environmental pollution and its effects were most pervasive. Garbage and filth of every kind were thrown

into the streets, covering the surface, filling the gutters, and often clogging the sewers. In the winter, the filth and garbage would accumulate in the streets to depths of several feet. Most cities were nightmares of primitive sanitation that lacked adequate waste disposal systems. Privies for sewage and private wells for water lacked safe separation distances and were still widely used in metropolitan areas until the end of the nineteenth century.

Many have argued that the national government could have done more to protect both the land and its resources as well as public health. But, for most of the nineteenth century, the government was still a weak presence in most areas of the country. There was, moreover, no body of laws with which the federal government could assert its authority. *Laissez-faire* was the order of the day. By the end of the nineteenth century, there was a growing body of information about the harm being done and some new ideas on how to correct these problems. Yet, there was no driving force to compel people to treat the land, air, and water with wisdom and care. To a large extent, people simply did not realize what they were doing [5].

As the nineteenth century was drawing to a close, three very special individuals made their entrance on the national scene. Gifford Pinchot, John Muir, and Theodore Roosevelt were to write the first pages of modern environmental history in the United States. Their efforts led to the birth of the modern environmental movement early in the twentieth century. However, pollution and environmental degradation was a major fact of life across most of America during the first half of the twentieth century, with phrases such as “the smell of money,” “good, clean soot,” “God bless it,” “it’s our life-blood,” and “an index to local activity and enterprise,” often used to describe this widespread environmental degradation.

The federal government ultimately entered into the environmental and conservation business in a fairly significant fashion when Teddy Roosevelt’s second cousin, Franklin, entered the White House in 1933. It was his political ideology, as much as his love of nature, that led Roosevelt to include major conservation projects in his New Deal reforms. The Civilian Conservation Corps, the Soil Conservation Service, and the Tennessee Valley Authority were among the many New Deal programs created to serve both the land and the people.

At this point in time, muscle and animal power were replaced by electricity, internal-combustion engines, and nuclear reactors. At the same time, industry was consuming natural resources at an incredible rate. All of these events began to escalate at a dangerous rate after World War II. In the late summer of 1962, a marine biologist named Rachel Carson, author of *Silent Spring*, the best-selling book about the damage to ecosystems being wrought by the overuse of pesticides, opened the eyes of the world to the potential dangers of attacking the environment with synthetic chemicals. It was perhaps at this point that America began calling in earnest for reform of the destruction of nature and constraints on environmental degradation. Finally in the 1970s, Congress began creating

environmental laws that addressed these issues, beginning in 1970 with the birth of the U.S. Environmental Protection Agency (EPA), details of which are provided in Chapter 5.

Paustenbach [6] provides additional details on

1. Occupational disease recognition (1900–1930)
2. Toxicology studies and risk assessment (1930–1940)
3. Concern over low-level health risks (1940–1950)
4. Setting acceptable daily intakes (1950–1970)
5. The cancer hazard (1970–1985)
6. Recent concerns regarding risk assessment

For literature regarding Early History and the Environmental Movement, the interested reader is referred to the book by Philip Shabecoff titled *A Fierce Green Fire* [5]. This outstanding book, as well as Ponting's *A Green History of the World* [3], is a “must” for anyone who works in or has interest in the environment.

Illustrative Example 2.1

Is falling down the stairs a health problem?

Solution

Based on the definition provided in the previous chapter, it is *not* a health problem. This “event” is best characterized as an *accident* or *hazard*.

Illustrative Example 2.2

Were there rules and regulations related to environmental concerns before the EPA was founded?

Solution

The answer is *yes*. Some of the earlier laws are discussed in Chapter 5.

Illustrative Example 2.3

Which is more important from a risk perspective, the location of the agent or the exposure to the agent?

Solution

As the reader will soon find out, each is equally important. Furthermore, *both* the presence of an agent and exposure to it have to occur for an environmental health risk to exist.

Illustrative Example 2.4

Is dichloro-diphenyl-trichloroethane (DDT), a chemical, to be concerned about?

Solution

It depends on whose argument you consider. In 1962, Rachel Carson, an opponent of the overuse of pesticides, succeeded in widely spreading information about DDT's affects on wildlife and humans, especially children. According to Levin [7], however, DDT's earlier usefulness in combating malaria and other insect-borne diseases was unprecedented, claiming that millions (perhaps hundreds of millions) were saved by DDT. In effect, Levin claimed that Carson failed to apply appropriate/applicable cost/benefit analyses to the issue, particularly when considering that malaria had caused the death of millions of children in under-developed countries. Although the jury is still out, the world health community has revisited the benefits of DDT. In fact, the DDT question will be addressed in Part II, Chapter 8 [8].

Illustrative Example 2.5

Are there other health and health-related problems that society will be concerned about in the future?

Solution

Two areas of future concern from a health and environmental safety perspective (and they are major) include

1. The looming clean water shortage
2. Clean and sustainable energy production

Providing extensive details of these two problems is beyond the scope of this chapter.

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3

History of Environmental Hazard Problems

3.1 Introduction

Whether a careless mishap at home, an unavoidable collision on the freeway, or a miscalculation at a chemical plant, accidents are a fact of life. Even in prehistoric times, long before the advent of technology, a club-wielding caveman could swing at his prey and inadvertently topple his friend in what can only be classified as an “accident.” As humanity progressed, so did the severity of these misfortunes. The “modern era” has brought about assembly lines, chemical manufacturers, nuclear power plants, and other technological complexities, all carrying (to differing degrees) the capability of disaster. To keep pace with the changing times, safety precautions must constantly be upgraded. It is no longer sufficient, as with the caveman, to shout a warning “Watch out with that thing!” Today’s problems require more elaborate systems of warnings and controls to minimize the chances of serious accidents.

This chapter examines the history of accidents from early incidents to recent catastrophes. In conjunction with this review, the material will cover the evolution of safety precautions, particularly as they apply to chemical plants. A crucial part of any design project is the inclusion of safety controls. Whether the plans involve a chemical plant, a nuclear reactor, or a thruway, steps must be taken to minimize the likelihood or consequences of accidents. It is also important to realize how accident planning has improved in order to monitor today’s advanced technologies. This chapter reviews a variety of actual accidents in order to provide an understanding of these phenomena, which, in turn, will supplement the subsequent chapters that deal with these subjects in significant technical detail.

The remainder of this chapter addresses the following topics:

- Early accidents
- Recent major accidents
- Major accidents in the twenty-first century
- Advances in safety features

3.2 Early Accidents

Accidents have occurred since the birth of civilization. People who learned from accidents survived to reproduce, and those who did not were unable to “fight another day.” Accidents were just as damaging in early times as they are today. Anyone who crosses a street or swims in a pool runs the risk of injury through carelessness, poor judgment, ignorance, or other circumstances. This has not changed through history. In the following pages, a number of accidents and disasters are examined that took place before the advances of modern technology. Catastrophic explosions have been reported as early as 1769, when one-sixth of the city of Brescia, Italy, was destroyed by the explosion of 100 tons of gunpowder stored in the state arsenal. More than 3000 people were killed in this, the second deadliest explosion in history. The worst explosion in history occurred in 1856 on the Greek island of Rhodes. A church, which had gunpowder stored in its vaults, was struck by lightning. The resulting blast is estimated to have killed 4000 people. This remains the highest death toll in recorded history for a single accidental explosion [1].

3.2.1 Great Chicago Fire

One of the most legendary disasters occurred in Chicago in October 1871. The “Great Chicago Fire,” as it is now known, is alleged to have started in a barn owned by Patrick O’Leary when one of his cows overturned a lantern. The O’Leary house escaped unharmed, since it was upwind of the blaze, but the barn was destroyed as well as 2124 acres of Chicago real estate.

The Chicago fire may be blamed on a farmer’s cow; however, the reason for the extent of the damage was the city’s shoddy construction. Almost all the buildings and houses were built of wood, and many of the sidewalks and roads were also of wooden construction. The streets were dangerously narrow, allowing flames to easily leap across to neighboring structures. The water supply proved to be inadequate, despite the location of Chicago on the banks of Lake Michigan. Add to this the extended drought conditions of the summer of 1871, which had earlier caused numerous smaller fires, and all the elements of a catastrophe were present.

Chicago was clearly unprepared for the events that took place on that day. The city was planned and constructed with little apparent regard to safety or fire prevention. No emergency plan was implemented, and panic was the order of the day, with people grabbing whatever possessions they could carry and fleeing the city. Looters and thieves broke store windows and helped themselves. All told, between 200 and 250 people were killed, another 200 were reported missing, and 100,000 were left homeless. The total loss of property was estimated in excess of \$200 million, forcing more than 60 insurance companies into bankruptcy. Whether or not O’Leary’s cow

actually caused this massive fire, the fact remains that accidents often occur under the most unlikely circumstances [2].

3.2.2 South Fork Dam: Johnstown, Pennsylvania

On May 31, 1889, an accident occurred that took the lives of 2209 people. The site was in Johnstown, Pennsylvania, and the incident was a flood that followed the collapse of a dam. The South Fork Dam was originally constructed to provide water for a proposed canal system between Johnstown and Pittsburgh. After the dam was completed, however, the project was abandoned. The dam changed ownership several times and eventually became the property of a group of rich industrialists who stocked the lake with fish and installed wire-mesh grates over clogged canals, decreasing the drainage capacity of the dam. Structural engineers warned that the dam was destined to collapse, but the warning went unheeded.

In the spring of 1889, unusually heavy rains caused the water level of the lake to rise, which caused the dam to rupture on May 31. A wall of water 40 ft high crashed down into the valley and the city. The lake drained at a rate of 200,000 ft³/s, and the entire lake was emptied in 36 min. The rushing wave picked up houses, trees, people, and debris. The flood was stopped when a bridge over the Conemaugh River caught most of the debris, forming a natural dam. Eventually, the rushing water sputtered out, and the danger was over. Although this disaster appears to be a clear case of negligence, it was deemed an “act of providence” and no damages were ever paid by the dam owners.

In the Johnstown flood case, there was no adequate evacuation or safety plan. Once the dam had broken, the water reached the city in a matter of minutes—hardly enough time for a city to react. However, the warnings of inspectors should have been taken seriously. Johnstown, a city of 30,000 people, was destroyed because of the carelessness and ignorance of a few [1].

3.2.3 Oppau, Germany

As technology advanced, large factories began growing throughout the world. Chemical manufacturers were called upon to supply an increasing number of products. These changes brought about new potential dangers. One such danger became a reality in Oppau, Germany, on September 21, 1921. Early in the morning, two massive explosions shook the surrounding area. Damage was reported 53 miles away in Frankfurt, while the shock was felt as far as 145 miles away. More than 700 houses were destroyed in the village of Oppau, and approximately 500 people died. Many lives were spared because the blast blew walls and roofs of houses away rather than knocking them down on the occupants. The cause of the blast was the sudden explosion of 4500 tons of ammonium sulfonitrate, an ammonium salt.

Specific details regarding the accident and its causes are sparse because, as is usually the case in such a mammoth disaster, none of the plant operators present at the time survived the incident. The large buildings containing the ammonium sulfonitrate disappeared entirely, and nothing was left in their place except a crater 250 ft in diameter and 30 ft deep. Ammonium sulfonitrate had never been known before to explode or to ignite spontaneously. This compound forms a hard mass when stored in large quantities, which was usually blasted apart with dynamite to prepare it for transportation. However, this technique, which had been used thousands of times without serious incident, was apparently responsible for the explosion in Oppau. It had been noted that the salt had changed from its original white color to a slightly yellow color and that the temperature of the storage rooms had risen 20°C above normal. These conditions may have led to a partial decomposition of the stored material to ammonium nitrate, which caused spontaneous ignition of the mass present.

The Oppau explosion came about because of a lack of understanding of the chemical being manufactured. Although there had been no earlier reported incidents of ammonium sulfonitrate exploding, a similar compound, ammonium nitrate, is known to be highly explosive. Thus, a more careful examination of this compound's characteristics should have been conducted. In addition to performing more research, management could have developed a method of breaking up the hardened mass other than blasting it with dynamite. Many lives were lost because a company decided to cut corners [3].

3.2.4 East Ohio Gas Company: Cleveland, Ohio

Some accidents can be attributed to structural failures. On October 20, 1944, one of the four liquid natural gas tanks at the East Ohio Gas Company in Cleveland began to leak. The plant converted natural gas to the liquid form, which was stored for emergency use in holding tanks. If needed, the liquefied product could be reconverted to its gaseous state and fed into the city distribution lines. The tanks were constructed in 1941 and had a capacity of more than 400,000 ft³ of liquid.

At the time of the disaster, the leaking liquid escaped into the plant grounds and beyond, vaporizing as it traveled. A spark or flame ignited the highly combustible gas, causing a drawback and fire that quickly engulfed the tanks and plant itself. Almost before the 80 gas company workers knew what was taking place, an explosion blasted out walls and flattened structures in the plant, killing the entire work force. The fire spread quickly through the district, destroying 52 homes and damaging 200 others. Four industrial plants were leveled and 20 others were damaged; 131 people were killed, 72 being burned beyond identification and buried in a common grave. The extent of the disaster was greatly increased by the location of the

plant, which was close to a residential area. In fact, this case is still used as an argument against the siting of liquefied natural gas facilities in urban areas [4].

As was the case in Oppau, Germany, in 1921, everyone with firsthand knowledge of the disaster was killed on the site, leaving the cause of the incident unknown. It is reasoned that a structural weakness in one of the tanks caused the gas leak, although the liquefied gas was not under any pressure. The tanks were only 3 years old when the accident occurred and certainly were not expected to develop any leaks. Although it is difficult to say how often plant structures should be inspected, one would reason that it should be possible to use a new tank with the assurance that it is structurally sound.

3.2.5 Texas City, Texas

Catastrophic accidents have occurred at sea as well as on land. In 1947, an unusual incident involved both. The French freighter *Grandcamp* arrived at Texas City, Texas, to be loaded with 1400 tons of ammonium nitrate fertilizer. During the night, a fire broke out in the hold of the vessel, but apparently fearing that water would damage the rest of the cargo, the crew made only limited attempts to fight the flames. Since the *Grandcamp* was docked only 700 ft from the Monsanto chemical plant, which produced styrene, a highly combustible ingredient of synthetic rubber, the *Grandcamp* was ordered to be towed away from the harbor. As tug boats prepared to hook up their lines, the *Grandcamp* exploded in a flash of fire and steel fragments. The blast rattled windows 150 miles away, registered on a seismograph in Denver, and killed many people standing on the dock. The Monsanto plant exploded minutes later, killing many survivors of the first blast, destroying most of the Texas City business district, and setting fires throughout the rest of the city. As the fires burned out of control, the freighter *High Flyer*, also loaded with nitrates, exploded in the harbor.

This third explosion was too much for the people of Texas City, who had responded efficiently to the initial two blasts. Hundreds were forced to leave the city, letting the fire burn itself out. The series of explosions had killed approximately 500 people and seriously injured 1000 others. The final death toll may have been as high as 1000 because the dock area contained a large population of migrant workers without permanent address or known relatives. It was reported that this disaster probably was caused by careless smoking aboard the *Grandcamp* [1,2].

Illustrative Example 3.1

What were the factors contributing to the spread and severity of the Chicago fire of 1871?

Solution

1. Shoddy construction of the city. Most of the houses and buildings were made of wood.
2. Narrow roads allowed flames to leap across the streets and spread to other areas; the winds of the “windy city” also contributed to the severity of the disaster.
3. Inadequate water supplies and existing drought conditions allowed limited response to be mounted against the blaze.
4. The city was completely unprepared for the event. There was virtually no evacuation or safety plan developed to respond to such incidents.

3.3 Recent Major Accidents

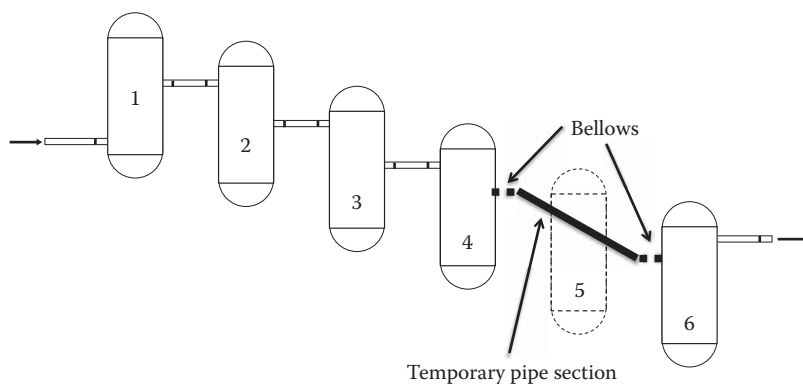
The advances of modern technology have brought about new problems. Perhaps the most serious of these is the threat of a nuclear power plant accident known as a meltdown. In this section, several of this era’s most infamous accidents, both at nuclear power plants and chemical plants, are examined, and some possible explanations for their occurrence are also offered.

3.3.1 Flixborough, England

An explosion at the Nypro Ltd. caprolactam factory at Flixborough, England, on June 1, 1974, was one of the most serious in the history of the chemical industry and the most serious in the history of the United Kingdom. Of those working on the site, 28 were killed and 36 others injured. Outside the plant, 53 people were reported injured, while 1821 houses and 167 shops suffered damage. The estimated cost of the damage was well over \$100 million.

The oxidation plant at Flixborough, which stored cyclohexane at about 120 psig and 145°C, contained six reactors in series (see Figure 3.1). One reactor had been removed for repairs, and the resulting gap was bridged by a temporary 20 in. diameter pipe, connected by a bellows at each end and supported on temporary scaffolding. This pipe collapsed, and in the minute or so that elapsed before ignition, about 35 tons of cyclohexane escaped. The extensive damage that occurred could have resulted from the deflagration of as little as 10–20 tons.

It was later determined that no calculations had been performed to ascertain whether the bellows or pipe could withstand the strain. Instead, only the capacity of the assembly to carry the required flow was calculated. No reference was made to any accepted standard, nor to the designer’s guide issued by the manufacturer of the bellows. Neither the pipe nor the complete assembly was pressure tested before being fitted. Apparently no one realized

**FIGURE 3.1**

Reactor sequence at the Nypro Ltd. caprolactam factory at Flixborough, England.

that the pressurized assembly would be subject to a turning moment, imposing shear forces on the bellows for which the system was not designed. Nor did anyone appreciate that the hydraulic thrust on the bellows would tend to make the pipe buckle at the joints. This temporary pipe connection functioned satisfactorily after the initial installation. It was never closely inspected, however, even though (when at operating temperature and pressure) it was observed to lift off the scaffolding that had been put in place to support it [5,6].

What happened on the final shift will never be known because all those in the control room were killed, and all instrumentation and records were destroyed. The equivalent force of the explosion was estimated to have been at least 15 tons of trinitrotoluene (TNT).

This particular accident serves as a case study for a book by one of the authors titled *Chemical Reactor Design and Applications for the Practicing Engineer* that is currently in preparation for John Wiley & Sons.

3.3.2 Seveso, Italy

At least 220 persons were evacuated on July 26–28, 1976, from Milan's northern industrial suburb of Seveso where a chemical factory explosion released a cloud of trichlorophenol (TCP) gas into the atmosphere, containing the highly toxic defoliant, dioxin. Approximately 5 lb of dioxin was released. Used by U.S. forces in Vietnam, dioxin is known to cause liver and kidney damage and genetic alteration. Eighteen days after the leak, hundreds of rabbits, birds, cats, dogs, and chickens died. Plants withered, and nearly 30 people were hospitalized with skin rashes and internal disorders. A 172 acre contamination zone was enclosed with barbed wire while emergency plans were drawn up to evacuate an additional 15,000 people if the cloud spread. A decontaminant, consisting of water and olive oil, was field-tested

on August 28 at the site. Within 48 h of spraying the decontaminant, 70% of the dioxin had been eliminated. A government spokesman estimated total damages at more than \$48 million [7].

Details on the accident are somewhat sketchy, but the following details are now available. The process system included a reactor where 2,3,5-trichlorophenol (TCP) was being synthesized from 1,2,4,5-tetrachlorobenzene in a liquid mixture of NaOH, ethylene glycol, and xylene. As the reaction neared completion, the plant crew decided to leave for the weekend before completing the final processing step that included the addition of quench water. Because of this, the reactor system overpressurized and the pressure relief system expelled 2 kg of 2,3,7,8-tetrachlorodibenzopara-dioxin (the most toxic of all dioxins) from the reactor. The pressure relief system worked exactly as designed by preventing the explosion of the reactor; however, the relief went directly into the atmosphere. It was then dispersed by a wind across the countryside where children playfully thought it was "snowing." The disaster later ensued.

3.3.3 Three Mile Island, Pennsylvania

Moving to more complex technology, the best known of the U.S. nuclear accidents occurred in 1979 on Three Mile Island in Pennsylvania. A series of breakdowns in the cooling system of the plant's Number 2 reactor led to a major accident in the early morning hours of March 28. Two days later, the Nuclear Regulatory Commission (NRC) warned of a possible core melt-down, a catastrophic event that could involve major loss of life. The possible explosion of a hydrogen gas bubble that had formed in the overheated reactor vessel of the crippled plant was also a major threat. Because of concern over the continued emission of radioactive gases, pregnant women and pre-school children within a 5 mile radius of the plant were advised to leave the area. On April 2, there was a dramatic reduction in the size of the dangerous gas bubble, as well as further cooling of the reactor core. A week later the bubble had been eliminated.

The accident at Three Mile Island unfortunately threatened the future of nuclear power in the United States and called into question the safety systems required by the NRC and used by the nuclear power industry. At the time of the accident, 72 nuclear reactors provided 13% of the nation's electrical power.

The cause of the incident has been hotly contested by the plant's owners, Metropolitan Edison Company, the NRC, the State of Pennsylvania, and companies that had constructed elements of the reactor system. Apparently, what had happened was the failure of a valve in a pump in the primary core cooling system. In addition, there was human error. This interrupted the flow of water used to cool the reactor, which caused the steam turbine to stop and consequently shut down the reactor. However, the reactor continued to generate heat and, as a result, the emergency cooling system began operating

automatically. At some point during the switchover from the primary cooling system to the emergency core cooling system, a plant operator turned off the emergency system and, after a period of time, turned it back on. The core was damaged during that time. Some of the pellets of enriched uranium fuel became so heated that they either melted through or ruptured the zirconium-clad tubes that held them. Some of the water used to cool the core spilled onto the floor of the reactor building. When some of that radioactive water became steam, it was vented into the atmosphere to relieve pressure.

Vented steam was not the only source of radiation leakage. Radiation had also been traced directly to nuclear materials within the plant that had escaped by penetrating 4ft thick walls. The uranium fuel in the core remained so hot that the plant's managers had to vent more steam into the atmosphere to prevent an explosion in the containment building. The direct result of the venting was the release of small amounts of radioactive iodine, krypton, and xenon. The levels were described as "quite low" and not dangerous to humans. Fortunately, there was no *apparent* serious exposure of the plant's workers. The long-range effects, however, are not yet known. According to a professor of radiology at a local university, "It's not a disaster where people are going to fall down like flies. It's a creeping thing."

Federal safety investigators reported that a series of human, mechanical, and design errors had contributed to the Three Mile Island accident. Metropolitan Edison had taken three auxiliary cooling pumps off-line for maintenance 2 weeks before the accident and had kept them off-line—a major violation of federal regulations. Several other errors contributed significantly to the incident: electrical magnetic relief valves that had opened to release a buildup of water pressure in the reactor had failed to close as designed; plant operators received incorrect readings from the pressure level indicator about the amount of water in the reactor; and, on two occasions after the accident, operators prematurely shut off the emergency core cooling system. Also, the release of slightly radioactive water into the Susquehanna River and the venting of steam into the air had been done without NRC approval [7].

3.3.4 Chernobyl, Russia

Everyone's worst fears about nuclear power became a reality in the later part of April 1986. A large Soviet reactor—unit Number 4 at Chernobyl, 80 miles north of Kiev, and only 3 years old—blew out and burned, spewing radioactive debris over much of Europe. Radiation levels increased from Sweden to Britain, through Poland, and as far south as Italy. The damage caused to the environment far surpassed that due to the accident at Three Mile Island.

The sequence of events at the Soviet reactor appears to have been as follows: First, the reactor suffered a loss of cooling water that caused the uranium fuel elements to become overheated. The reactor had no containment building to keep in radioactive releases. Therefore, all the radioactivity generated in this stage of the accident entered the atmosphere. Eventually, the

temperature of the fuel rose to a point at which the graphite casing holding the uranium caught fire. Water could not be used to put the fire out because it would have evaporated, causing plumes of radioactivity to escape.

The explosion was the result of a series of errors by plant operators who were conducting an unauthorized experiment after having shut down the emergency cooling system. Operators were attempting to prove that if a turbine tripped in the event of a power outage and was disconnected from the steam supply, they would be able to draw kinetic energy from the still spinning rotor blades to operate emergency coolant pumps until the backup diesel generators began operating. Operators began to reduce the power output on April 25. Tests were conducted at 7% power, a level at which the plant is subject to automatic shutdown. At such low power levels, xenon gas builds up to absorb neutrons and slow the fission process. When this occurred at Chernobyl, it caused the loss of control of the reactor. Power dipped to as low as 1% before it was finally stabilized back to 7%. To increase the flow of water to the reactor, two additional cooling pumps, in addition to the six normally used, were engaged. The cooling water inside the reactor's pressure tubes was already close to boiling or had reached that point because the drop in pressure from the low power output had heated the coolant. When the turbine was tripped, the coolant turned to steam. Unfortunately, heat could not escape because emergency systems had been shut off. Power began to surge as the water dissipated in the reactor. A heat buildup caused the zirconium casing to react with the water, releasing hydrogen. Two explosions occurred, blowing the roof off the reactor building, destroying the cooling system, and severely damaging the core.

The accident reportedly killed 31 people, injured 299 others, and caused the evacuation of 135,000 from the site. The full extent of the damage from this incident probably will not be known for years. It is the long-term effects from exposure to radiation that frighten most people, and these fears may still become a horrible reality [8–11].

Nuclear accidents, while being the most frightening, have not occurred often. In fact, there have been only a handful of fatal incidents since an understanding of nuclear energy and radiation has been developed. However, pioneers of radiation research, including Marie Curie, are known to have died from radiation poisoning because they neglected to effectively control their exposure to this powerful energy source. Today, a better understanding of the risks associated with radioactive materials has led to fewer careless deaths. However, as Chernobyl proved, industry is far from having perfected the science of using nuclear energy.

Although much still remains to be learned about the interaction between ionizing radiation and living matter, more is known about the mechanism of radiation damage on the molecular, cellular, and organ system level than most other environmental hazards. A vast amount of quantitative dose-response data have been accumulated throughout years of studying the different applications of radionuclides. This information has allowed the

nuclear technology industry to continue at risks that are generally no greater than any other technology.

3.3.5 Bhopal, India

As discussed earlier, nuclear power plants have not been the only industrial sites of major accidents in recent times. Other disasters at chemical plants have been responsible for a much greater loss of life. The worst disaster in the recent history of the chemical industry occurred in Bhopal, in central India, on December 3, 1984. A leak of methyl isocyanate (MIC) from a chemical plant, where it was used as an intermediate in the manufacture of a pesticide, spread into the adjacent city and caused the poisoning death of more than 2,500 people; approximately 20,000 others were injured.

The owner of the plant, Union Carbide Corporation, reported that the accident was "the result of a unique combination of unusual events." The MIC was driven out of a storage tank by pressure generated from a water-induced runaway polymerization reaction. The last batch of MIC put into the tank before the accident contained more chloroform than the product specifications allowed. Chloroform promotes the polymerization of MIC although chloroform alone cannot react without the high temperatures caused by the presence of water. The excess chloroform is one of the "unusual events" preceding the disaster, although the presence of water appears to be the primary culprit.

The most intriguing question is why the plant's safety equipment and controls, which should have been designed to cope with a chemical that is known to be subject to violent reactions, did not work. The MIC tank had three safety devices. A pipe leading from the tank contained a valve that was set to rupture if the pressure in the tank exceeded 40 psi. Beyond the valve, there were two other safety devices. One was a flare (tower) to burn escaping gas. The other was a vent gas scrubber, a tower packed with loose material through which a solution of caustic soda could be poured onto rising MIC to decompose it. On December 3, 1984, the operator of the factory's control room noticed that the pressure in the MIC tank had risen from 2 to 30 psi, and in a matter of a few minutes, it had risen above the gauge maximum of 55 psi. The tank was hot and rumbling, its concrete cladding was cracking, and the safety valve was screeching. The flare was shut down for maintenance, so the operator turned on the vent gas scrubber. The flow meter failed to indicate that a flow of caustic soda had started. However, the morning after the accident, the scrubber's runoff solution was hot, which indicated that the scrubber had worked and the pump had operated properly. When the flow meter was subsequently cleaned, it started working properly. This is one indication that maintenance at the plant was poor. Other evidence indicates that the concentration of the caustic solution had not been tested since the previous October. Despite this, the scrubber seems to have worked normally on the

night of the accident. However, the scrubber was not able to control the entire release of MIC. After it had been operating for 45 min, the plant superintendent verified that MIC was being released into the atmosphere from the scrubber stack.

In addition to the failings of the safety system, the most pressing question was how the water made its way into the MIC tank in the first place, causing the fatal reaction. Obviously, the plant could not contain a runaway reaction, and an investigation proved that water alone caused the Bhopal disaster. The Union Carbide Corporation has cited some evidence that points to sabotage, and not plant mismanagement, as the cause of the disaster [12]. Their scenario, based on this evidence, is that a disgruntled worker sneaked into the deserted storage area, removed the pressure gauge on one tank, attached a water hose to the opening, and turned on the faucet. A chain of chemical reactions ensued and the pressure and temperature in the tank began to build. The MIC vaporized at the higher temperature and forced its way past the relief valve, through the pipeline, and into the vent tower. Several hours later, some workers noticed the odor of MIC gas and, while searching for a leak in the storage area, found the hose. It is believed that they attempted to siphon off the water by transferring it to another unit. Ten minutes later, the gas began leaking more rapidly. In an attempt to cover up the error, the workers' logs were altered to show that the transfer took place before the water was introduced into the tank. Evidence for this scenario exists in the testimony of a former employee who stated that a pressure gauge was missing from the storage tank the morning after the disaster. Additionally, shortly after the accident, several workers mentioned that water had been intentionally added to the tank. It was difficult to follow up this claim because the workers were dismissed and could not be found after the plant closed [12].

At the time of the accident, many people wondered why a chemical plant that produced such a dangerous compound was located so close to a residential area. The plant was originally built 1.5 miles from the nearest housing area, but a small town grew up next to it. Zoning laws in many countries would have prevented such development. The Bhopal tragedy reinforces the need for controls to prevent the siting of plants that produce hazardous chemicals close to residential areas and to prevent residential construction close to these plants.

The chemical produced at Bhopal, MIC, is an intermediate in the manufacturing of Carbaryl, which accounts for only 3% of all the pesticides used today. This accident suggests that perhaps, whenever feasible, industry should develop plants that use less hazardous raw materials in their manufacturing process. Most plants are made safe by adding protective equipment, which, as in the Bhopal incident, may sometimes fail or prove inadequate. However, if a plant does not use or produce hazardous materials, the probability of such an accident is very low. Developing new and safer designs can, in the long run, be more economical than trying to control the

hazards associated with older designs [13–16]. This pollution prevention/green chemistry concept is discussed in more detail in Illustrative Example 3.4 and in Part III.

3.3.6 Ashland Oil, Pennsylvania

An accident occurred on January 2, 1988, that did not involve the loss of human life but nevertheless can be considered to be a major industrial disaster when a 48 ft high fuel tank ruptured at the Ashland Oil terminal in southwestern Pennsylvania. Nearly 3.9 million gallons of Number 2 distillate fuel was catastrophically released from the tank, the force of which caused the tank to jump backward 100 ft and sent a 35 ft high wave of fuel crashing into another tank 100 ft away. A containment dike trapped much of the spilled fuel. However, 600,000 gal escaped into the Monongahela River at Floreffe, about 25 miles upstream from Pittsburgh. Soon after the spill, a rumor began circulating that there was a possible gasoline leak as well. This raised concerns about a fire, leading to the evacuation of 250 homes.

Although the containment dike was large enough to hold the entire contents of the tank, the tank ruptured so suddenly that the release generated a wave of fuel oil that splashed over the embankment. The tank, 56 ft high and 120 ft in diameter, was erected in 1986 on a newly enlarged concrete foundation that previously had supported a smaller vessel. The tank was constructed of 40 year old steel, which presumably contained less carbon and was more brittle than newly manufactured steel.

In addition, the tank had been moved from a terminal near Cleveland and reassembled at the Ashland Oil site. To facilitate the move to Pittsburgh, the tank was cut both vertically and horizontally at the original welds, and then restacked in eight rings above a concave steel floor at the new site. This procedure has been questioned. Some experts contend that, for reasons of structural integrity, the tank should not have been cut horizontally.

Ashland also admitted that the usual testing procedures were not employed before putting the tank into service. Hydrostatic testing is recommended by the American Petroleum Institute (API), but pumps large enough to raise water to the top of the tank were not available at the site. An alternate procedure was performed in which the tank was sprayed with diesel fuel and subjected to a vacuum. However, the tank was not inspected by any outside agency prior to its use.

The fuel that had spilled into the frigid water began to emulsify and sink, and the extremely cold weather at the time of the release caused ice to form on the river. It is nearly impossible to recover oil that sinks below the skirts of the recovery booms or that becomes trapped under ice. However, various methods were used to remove the oil from the Monongahela. Chemists developed a method that mixed the contaminated water with powdered

carbon and bentonite, which gives the slurry higher absorbency. The mixture is then pumped to a treatment plant where other chemicals are added to balance acidity and make the oil coagulate in a settling tank. This treatment is not new, but the chemists had to come up with the right combinations of chemicals to handle the oil. At one point, the EPA allowed the use of a substance called *Elastol* for the first time. *Elastol* congeals spilled hydrocarbons into a mass that can be easily recovered.

Although an accurate assessment could not be made immediately, the Ashland spill took a heavy toll on the wildlife of the Ohio River Valley. More than 5000 waterfowl were killed when their feathers became contaminated with oil. Birds that experience oil contamination lose their natural insulation and buoyancy and either drown or freeze to death. In addition, a massive fish kill was anticipated in the spring when the ice thawed and increased flow in the river increased the release of residual oil into the aquatic ecosystem.

The Pittsburgh area was the hardest hit by the spill. Two communities with a combined population of 23,000 were completely without water for 5 days, and many others were left with critically short supplies. To alleviate the problem, workers constructed a 12 in. diameter line to connect an unaffected city water system, which drew its supply from the Allegheny River, to the devastated Western Pennsylvania Water Company system.

This massive spill of oil jeopardized the water supplies of more than a million people as it moved downstream into the Ohio River through Pennsylvania, Ohio, and West Virginia. While 19,000 spills are reported each year, there has been only one other complete tank collapse in the past 20 years. Many still question whether more stringent regulation is needed for these large fuel storage tanks. They point to the need for more site-specific plans for spill prevention and control. The plans that facilities are required to file now tend to be more "generic." New legislation regulating a tank's proximity to storm sewers, waterways, and other facilities, as well as requirements to tailor planned responses to possible weather conditions and configurations of terrain is needed [17–19].

3.3.7 Trans World Airlines: Long Island, New York

Accidents have also occurred in the "air," an area that would be classified as a transportation accident. An example of this is the Trans World Airlines Flight 800 from New York to Paris. On July 17, 1996, a Boeing 747 sat on the runway at J.F.K. airport for an extended period of time. The heat generated from the idle plane was sufficient to vaporize residual fuel in what was considered an "empty" fuel tank. This created a very dangerous, flammable mixture of fuel vapor and air. Approximately 10 min after departure from J.F.K. airport, TWA Flight 800 exploded in mid-air. The most likely source of ignition for the flammable mixture of fuel vapor and air was an electrical

wiring problem. All 230 people aboard perished when the jet crashed off the coast of Long Island, New York. However, this tragedy could have been avoided by preventing the flammable mixture in the fuel tank from developing in the first place.

In response to the TWA Flight 800 crash, the Federal Aviation Administration (FAA) has moved toward requiring airlines to pump nitrogen gas into empty fuel tanks to inert them and to keep the pressure inside the tanks above the vapor pressure of the fuel and, hence, keep the fuel from vaporizing. This action prevents a flammable mixture from developing inside the tanks. Unfortunately, it took the deaths of the 230 people aboard TWA Flight 800 to bring prior FAA philosophies under scrutiny that allowed aircraft to fly with flammable fuel tanks [20].

Illustrative Example 3.2

Briefly discuss the lessons learned from the accident in Flixborough, England.

Solution

As described earlier in this chapter, the incident occurred on June 1, 1974. Three major lessons learned were as follows:

1. Although the design of a process is important, carefully evaluating the safety of retrofit and temporary installations can play an important role in accident management.
2. Reduce inventories at plant site.
3. Industrial facilities should not be located near populated areas as risks from toxic vapors are generally lowered with increasing distance because of dispersion effects.

In 1985, the Canadian Chemical Producers Association (CCPA) released a pamphlet entitled, "Essential Components of Safety Assessment Systems." "Modifications to process or plant" was one of the topics discussed in this pamphlet. CCPA recommended a 12-element program (listed below) to formally examine and approve process conditions, whether permanent or temporary, prior to implementation.

1. Does the change involve any different chemicals that could react with other chemicals, including diluents, solvents, and additives already in the process?
2. Does the new proposal encourage the production of undesirable by-products either through the primary reaction, through side reactions, or through impurities in the new chemical components?
3. Does the rate of heat generation and/or the reaction pressure increase as a result of the new process scheme?

4. Does the proposed change encourage or require the operation of chemical processing equipment outside of its approved operating or design limits?
5. Does the proposal consider the compatibility of the new chemical component and its impurities with materials of construction?
6. Have the occupational health and environmental impacts of the proposed change been considered?
7. Has the proposed design for modifying the process facilities or conditions been reviewed by a qualified individual using effective techniques for analyzing process hazards, particularly when the modifications are being made in rush situations or under emergency conditions?
8. Has there been an on-site inspection by qualified personnel to ensure that new equipment was installed in accordance with specifications and drawings?
9. Have the operating instructions and engineering drawings been revised to reflect the modifications that have been made?
10. Have proper communications been made for the training of chemical process operators, maintenance personnel, and supervisors who may be affected by the modification(s)?
11. Have proper revisions been made to the process control logic and instrumentation set and alarm points, especially for computer control systems, to allow proper response to the modification(s)?
12. Have provisions been made to remove or completely isolate obsolete facilities in order to eliminate the chances for operator error involving abandoned equipment?

These 12 elements indicate the types of questions that should be asked when making changes to chemical and industrial processes. The exact questions are not as important as realizing that many questions have to be asked to ensure operator and facility safety following process modifications.

Illustrative Example 3.3

Briefly describe the lessons learned from the accident in Bhopal, India.

Solution

As described earlier in this chapter, the incident occurred on December 3, 1984. Four major lessons learned were as follows:

1. Investigations are essential.
2. Protection systems must be fully operational.
3. All process and chemistry alternatives should be examined.
4. Plants should not be located near populated areas.

Illustrative Example 3.4

Two dominate chemical reactions were occurring in the Bhopal plant using the MIC reaction to form carbaryl. Briefly describe these two reactions.

Solution

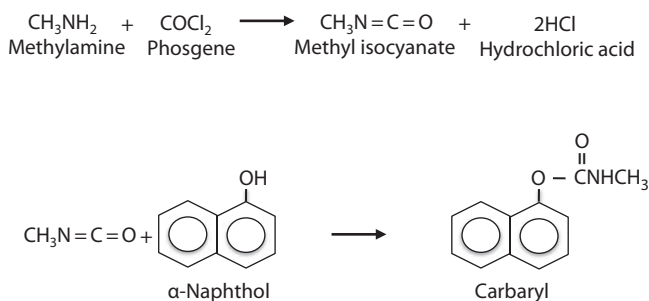
Two major chemical reactions were occurring in the Bhopal plant to produce carbaryl using MIC as an intermediate. The first of the consecutive reactions combined methylamine and phosgene to produce MIC and hydrochloric acid. The MIC then reacts with α -naphthol to form the final product, carbaryl. There is another possible route to produce carbaryl that does not make use of the MIC intermediate. Instead, phosgene is first reacted with α -naphthol to form α -naphthol chloroformate—the intermediate for the reaction—and hydrochloric acid. Then α -naphthol chloroformate in turn reacts with methylamine to form carbaryl and hydrochloric acid. Both reaction schemes (depicted in Figures 3.2 and 3.3) have the same overall stoichiometric equation, but the latter reaction is much more intrinsically safe as it does not involve the production of the very hazardous MIC intermediate.

Illustrative Example 3.5

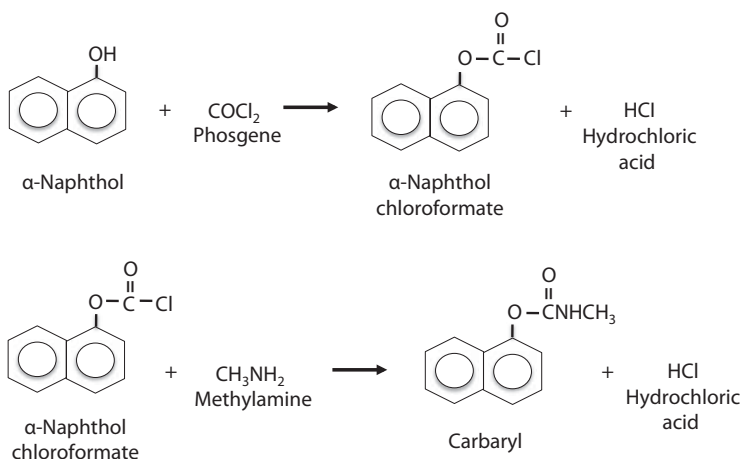
Briefly describe radioactive transformations, particularly as they apply to beta particle emissions.

Solution

Radioactive transformations are accomplished by several different mechanisms, most importantly alpha particle, beta particle, and gamma ray emissions. Each of these mechanisms is a spontaneous nuclear transformation. The result of these transformations is the release of energy and the formation of different and more stable elements.

**FIGURE 3.2**

Methyl isocyanate route.

**FIGURE 3.3**

Non-methyl isocyanate route.

The kind of transformation that will take place for any given radioactive element is a function of the type of nuclear instability as well as the mass–energy relationship. The nuclear instability is dependent on the ratio of neutrons to protons in the element; a different type of decay will occur to allow for a more stable daughter product. The mass–energy relationship states that for any radioactive transformation(s) the laws of conservation of mass and the conservation of energy must be obeyed.

Beta particle emission occurs when an ordinary electron is ejected from the nucleus of an atom. The electron (e) appears when a neutron (n) is transformed into a proton within the nucleus as demonstrated in Equation 3.1:



Note that the proton is shown as a hydrogen (H) nucleus. This transformation must conserve the overall charge of each of the resulting particles. Contrary to alpha emissions, beta emissions occur in elements that contain a surplus of neutrons. The daughter product of a beta emitter remains at the same atomic mass number but is one atomic number higher than its parent. Many elements that decay by beta emission also release a gamma ray at the same instant. These elements are known as beta-gamma emitters. Strong beta radiation is an external hazard because of its ability to penetrate body tissue [21].

Illustrative Example 3.6

How could the Ashland Oil accident have been prevented?

Solution

1. The tank should have been properly tested in accordance with API procedures, i.e., hydrostatic testing.
2. Ashland should have applied for a permit from the state to build the tank.
3. There should have been routine inspections by the employees.
4. The tank should have been built on a foundation suitable for a larger tank.
5. The steel used for the tank was of a poor quality; new steel should have been used.
6. Horizontal cutting of structural panels is not recommended for tanks and could have led to the structural failure of this tank.

Illustrative Example 3.7

What is a *core meltdown*? What was the probable cause of the Three Mile Island incident?

Solution

1. A core meltdown occurs when tubes holding uranium fuel melt or rupture due to the intense heat of the fuel rods. As a result, radiation is leaked and could be released to the environment.
2. The Three Mile Island incident was apparently caused by a failure of a valve in the primary core cooling system.
 - a. This interrupted the flow of water used to cool the reactor, which caused the steam turbine to stop, and consequently shut down the reactor. However, the reactor continued to generate heat, and, as a result, the emergency cooling system began operating automatically.
 - b. At some point during the switchover from the primary cooling system to the emergency core cooling system, a plant operator turned off the emergency system and, after a period of time, turned it back on. During that time the core was damaged.
 - c. Some of the water used to cool the core spilled onto the floor of the reactor building. When some of that radioactive water became steam, it was vented into the atmosphere to relieve pressure.

3.4 Major Accidents in the Twenty-First Century

The twenty-first century brought a rash of “new” accidents; and a few of the more memorable ones, including the earthquakes of 2010, are detailed in the following. Note that the 9/11 terrorist incident is not included.

3.4.1 Y2K

A recent example of the effects of poor planning is described by what has become known as the Y2K (Year 2000) computer bug. Computers work with numbers and a very important and widely used number in both computer hardware and software is the date, particularly the year. These data, like any other data used by a computer, are stored in the computer's memory. When computers first started being used in the late twentieth century (1960s) and programs were being written for them, computer storage—random access memory (RAM) and disk memory—was very expensive. In an effort to reduce the amount of memory required to store the year, only the last two digits of the year were used. This system worked fine until the Year 2000. On December 31, 1999, as the digits were to change from 99 to 00, the year was actually going to change from 1999 to 1900 (instead of 2000). This would affect every business that was linked to a computer, and the commotion and hysteria that surrounded the Y2K bug were due to the present age's dependence on computers. For example, it was feared that the government's computer system would print social security checks with amounts seen in the year 1900 and that banks would calculate dividends based on interest rates from the year 1900. The problems could have been catastrophic. Fortunately, the response to the "potential" Y2K disaster was effective in that most corrections or "patches" were made before the Year 2000. However, these corrections were costly and did require large amounts of money to be spent to make them [22].

3.4.2 The Indian Ocean Earthquake and Tsunami

The Indian Ocean earthquake was an undersea mega thrust earthquake that occurred in December 2004. This undersea or ocean quake triggered a series of devastating tsunamis along the coastlines in that area. Approximately 250,000 people were killed (in 14 countries) as coastal communities were inundated with waves up to 100 ft high. It has been referred to as one of the deadliest natural disasters in recorded history. Indonesia was the hardest hit, followed by Sri Lanka, India, and Thailand. The earthquake registered between 9.1 and 9.3 on the Richter scale, the second largest earthquake in recorded history. The quake also had the longest duration of faulting ever recorded—approximately 10 min; it caused the entire planet to vibrate and apparently triggered other earthquakes as far away as Alaska.

In terms of lives lost, this was one of the 10 worst earthquakes in recorded history. It was also the single worst tsunami in history. Computational details on earthquakes can be found in Chapter 20.

3.4.3 Katrina

The year 2005 brought hurricane Katrina and its disastrous impact on New Orleans. Interestingly, the city had been described earlier as "a disaster

waiting to happen.” On August 29, the hurricane caused floodwater levees to catastrophically collapse throughout the city. Entire neighborhoods were flooded. Fortunately, the “eye” of Katrina passed to the east of the city, subjecting it to hurricane conditions but spared New Orleans the worst impact. The storm surge severely taxed the city’s inadequate levee system built years earlier by the U.S. Army Corps of Engineers. Interestingly, a 2007 report prepared by the American Society of Civil Engineers (ASCE) concluded that two-thirds of the flooding in the city could have been avoided if the aforementioned levees had held. The official death toll from the high winds and flooding was 1464 people.

Looting, violence, and other criminal activities became a serious problem in the aftermath of Katrina. Security in New Orleans degraded quickly, with most of the attention focused on rescue efforts. Looting had spread throughout the city within days, often in broad daylight and in the presence of police officers. The situation deteriorated to the point where the entire police force was ordered to abandon the search and rescue mission and turn their attention toward controlling the widespread looting.

Regarding health effects, there was a concern that the prolonged flooding and exposure to petrochemical-tainted floodwaters would lead to an outbreak of health and health-related problems for those who remained in the city. In addition to the lack of food and water, dehydration, and food poisoning, there was also the potential for the spread of hepatitis A, cholera, tuberculosis, and typhoid fever, as well as mosquito-borne diseases leading to yellow fever, malaria, and West Nile virus. See Chapter 20 for calculational details on both hurricanes and floods.

3.4.4 2010 Earthquakes

It would be appropriate to define the year 2010 as the year of natural disasters. The natural disasters in this case were primarily earthquakes, with three major earthquakes rocking the planet that year. See also Chapter 20 for calculational details of earthquakes.

The January 2010 Haiti earthquake had a Richter scale magnitude of 7.0. The Haitian government reported that an estimated 230,000 people had died, 300,000 had been injured, and 1,000,000 had been made homeless as a result of the quake. They also estimated that 250,000 residences and 30,000 commercial buildings had collapsed or were severely damaged. It was the most severe earthquake to hit Haiti in 200 years. It should also be noted that construction standards are poor in Haiti; the country has no building codes. At the time of the preparation of this chapter, as much as 98% of the rubble from the quake remained uncleared. An estimated 26 million cubic yards remain, making most of the capital impassable. Thousands of bodies remain in the rubble. The number of people in relief camps is estimated at 1.6 million, and almost no transitional housing has been built. Most of the camps have no electricity, running water, or sewage disposal, and tents are beginning to fall

apart. Crime in the camps is widespread, especially against women and children. Although enough aid had supposedly been raised internationally (primarily from the United States) to provide each displaced family with \$37,000, the O'Reilly Factor (FOX News) has reported that little to none of this money has been delivered to its intended beneficiaries.

One of the largest earthquakes in recorded history destroyed houses, bridges, and highways in central Chile in late February and sent a tsunami rocking halfway around the globe. Chileans near the epicenter were tossed around as if shaken by a giant. The 8.8 magnitude quake was felt as far away as Sao Paulo in Brazil—nearly 2000 miles away. The full extent of the damage still remains unclear today as dozens of aftershocks shuddered across the nation.

The China earthquake in April registered 7.1 on the Richter scale and resulted in the deaths of hundreds of thousands. In Jiegu, a township near the epicenter, more than 85% of houses collapsed, while large cracks appeared in buildings still standing. Officials initially reported that 10,000 people were injured due to quakes that hit Yushu County in Qinghai Province. It was concluded that people died because of the collapse of cheaply constructed buildings in a poor region where it seems little regard had been paid to building codes that could have offered better protection to the people.

3.4.5 Chilean Mine Accident

Mine safety began with the founding of the Bureau of Mines in 1910. Mine accidents were defined at that time as those resulting in five or more deaths. It was the Monongah coal mine explosion in 1907, claiming 362 lives, that prompted Congress to create the Bureau of Mines in 1910 (Public Law 61-179). Mine accidents have declined dramatically in number and severity since the Bureau's inception, with mine accidents resulting in five or more deaths—a rare occurrence in modern mining operations.

The most recent accident (just before the preparation of this chapter) that received international attention also occurred in Chile. The drama of the rescue of 33 miners trapped in a collapsed mine was viewed on TV by nearly the entire world, and clearly demonstrated both the health and hazard risks miners are exposed to on a daily basis. Illustrative Examples 3.10 and 3.11 are based, in part, on this event. On a human interest level, Chilean miner Edison Pena carried a Chilean flag to the finish line of the New York City marathon only 3½ weeks after being rescued from his 69 day ordeal at the bottom of the San Jose mine.

3.4.6 BP Disaster

At the time of the preparation of this book, the “year of disasters” culminated in the BP accident in the Gulf. In the wake of the April 20, 2010,

British Petroleum Deepwater Horizon offshore oil rig explosion and the accompanying millions of gallons of oil that were released into the Gulf of Mexico from the damaged rig, the general subject of environmental risk suddenly took on a never-dreamed-of level of importance. How and why this disaster occurred is still being debated by engineers, scientists, politicians, regulators, and the average citizen. One thing that cannot be debated is that the BP rig catastrophe produced the worst environmental disaster in American history. Officials of not only BP but also Exxon Mobil, Conoco Philips, Shell, Chevron, etc., continue to insist the accident was an aberration and could not happen again. Really? The scientific community knows better since accidents are an integral part of life; discussions of this nature have to ultimately lead to the often misunderstood term referred to earlier as *RISK*.

This accident produced the largest oil slick in the Gulf of Mexico since 1979. The leak was stopped (plugged) in July, shortly before the time of the initial preparation of this chapter. However, field personnel were still attempting to determine what happened to the oil rig as a blowout tore it apart, killing 11 of 126 men on board and depositing oil on the coastlines of Florida, Louisiana, Alabama, and Mississippi.

It is now estimated that the massive spill will cost nearly \$20 billion to clean up. The spill may exceed the 11 million gallons of oil released by the Exxon Valdez when it ran aground on the Bligh Reef in Prince William Sound in Alaska. At the time of preparation of this section, the Valdez remains the largest oil spill in U.S. history. (The largest global oil spill occurred during the 1991 Gulf war when the Iraqi army destroyed tankers, oil terminals, and oil wells in Kuwait, releasing 500 million gallons of oil to the environment.) It should be noted that the Gulf of Mexico provides America with much of its energy needs, accounting for approximately one-third of America's oil production.

The subject of emergency preparedness and response (see Chapter 6) has also surfaced in the aftermath of the Deepwater Horizon accident. Immediately following the BP disaster, steps were taken to not only prepare for the environmental effects associated with the massive release that occurred but also institute programs and actions to help reduce (or possibly eliminate) the probability of this occurring again. For example, the oil from the blown-out deepwater well had the potential (at that time) to move up the Atlantic coast and ultimately reach Long Island (home to one of the authors) beaches and local estuaries. The direction of the wind ultimately determined the quantity and the direction of oil migration. However, Nassau County worked with New York City in tracking the migration of the spill. In addition to tracking the spill, the county is now in partnership with other municipalities in drafting an Oil Spill Response Plan to address any local impacts. See Chapter 21 for calculational details on offshore rig accidents.

Illustrative Example 3.8

Was the earthquake in Chile in 2010 worse than the earthquake that occurred there in 1960?

Solution

The largest earthquake ever recorded struck near the same area of Chile on May 22, 1968, as the quake that occurred in February 2010. The 9.6 Richter magnitude quake killed a reported 1655 people and left 2 million homeless. It also caused a tsunami that killed people as far away as Hawaii, Japan, and the Philippines and caused damage along the west coast of the United States.

Illustrative Example 3.9

What were the other effects associated with the earthquake in Chile in February 2010?

Solution

This earthquake caused a surge of ocean water that traveled across the Pacific, prompting warnings across all 53 nations ringing the Pacific Ocean. Tsunami waves did reach Hawaii, but little damage was reported. Tsunami waves struck Japan's outlying islands the following day but, as with many of the other Pacific islands, they were spared major damage.

Illustrative Example 3.10

The data in Table 3.1 on mining accidents in Chile were recently published by Sernageomin, the National Geologic and Mineral Service of Chile. The mining industry in Chile currently involves 42 mine/processing sites and a total of 175,000 mine workers. Based on the data given in Table 3.1 for the last 10 years of accident statistics, determine the following:

1. Calculate the annual risk of mining injuries in units of injuries/miner, and injuries/million man-hours worked.
2. Determine the annual risk of mining deaths in units of deaths/miner, and deaths/million man-hours worked.

Solution

The average accident rate over the last 10 years in the Chilean mining industry expressed as average accident/year, average deaths/year, and average man-hours worked/year is:

30 accidents/year, 1789 injuries/year, 35 deaths/year, and 283 million man-hours worked/year.

TABLE 3.1

Historical Chilean Mining Data, 1997–2010

Year	Number of Mining Accidents	Number of Mining Injuries	Number of Mining Deaths	Million Man-Hours Worked
1997	43	3211	49	227
1998	33	2248	38	239
1999	17	1607	19	203
2000	32	1452	37	205
2001	30	1917	34	227
2002	25	2030	28	240
2003	26	1767	30	233
2004	29	1877	33	256
2005	26	1869	30	286
2006	27	1679	31	284
2007	35	1872	40	321
2008	38	2021	43	361
2009	31	1391	35	354
2010	36	1800	40	350

Average annual risk of a mining (AAR)-related injury:

$$(\text{AAR})\text{-related injury} = \frac{1,789 \text{ injuries/year}}{175,000 \text{ miners/year}} = 0.01 \text{ injuries/miner}$$

$$(\text{AAR})\text{-related injury} = \frac{1789 \text{ injuries/year}}{283 \text{ million man-hours worked/year}}$$

$$(\text{AAR})\text{-related injury} = 6.25 \text{ injuries/million man-hours worked}$$

$$(\text{AAR})\text{-related deaths} = \frac{35 \text{ deaths/year}}{175,000 \text{ miners/year}} = 0.0002 \text{ deaths/miner}$$

$$(\text{AAR})\text{-related deaths} = \frac{35 \text{ deaths/year}}{283 \text{ million man-hours worked/year}}$$

$$(\text{AAR})\text{-related deaths} = 0.12 \text{ deaths/million man-hours worked}$$

Illustrative Example 3.11

Comment on the results of the previous example.

Solution

The Chilean mining industry is one of the safest in the world due in large part to the influence of foreign mining interests in mining activities there. The recovery of the 33 Chilean miners in the San Jose mine in October 2010 can also be seen to have helped mitigate a sharp rise in Chile's mining death rate for 2010. The death rate calculated for Chile of 0.12/million man-hours worked is just twice that of the United States with a rate of 0.06/million man-hours worked in 2010. This is contrasted to the Chinese mining industry that has a death rate four times that of the United States and twice that of Chile at 0.24/million man-hours worked. With a very large and growing mining industry in China, even this low death rate, normalized to man-hours worked, represents 6027 mine worker deaths in China in 2004 alone.

It should also be noticed from the data provided that the injury rate is much higher than the death rate and reflects a large injury to death ratio ($>50/1$) (thankfully!) in the Chilean mining sector common to many industries.

3.5 Advances in Safety Features

Today's sophisticated equipment and technologies require equally sophisticated means of accident prevention. Unfortunately, the existing methods of detection and prevention are often assumed to be adequate until proven otherwise. This approach to determining a technology's effectiveness sometimes is costly and often leads to loss of life. Chemical manufacturers and power plants are businesses and thus are not as likely to "unnecessarily" update their present controls. Table 3.2 lists accidents, all of which have resulted in substantial loss of life, and the changes in safety-related practices they brought about [23].

Before the advent of technology, there was still a need for safety features and warnings; yet these did not exist. Many accidents occurred because of a lack of knowledge of the system, process, or substance being dealt with. Many of the pioneers of modern science were sent to an early grave by their experiments. Karl Wilhelm Scheele, the Swedish chemist who discovered many chemical elements and compounds, often sniffed or tasted his finds. He died of mercury poisoning. As noted earlier, Marie Curie died of leukemia contracted from overexposure to radioactive elements. Had either of these brilliant scientists a complete idea of the properties of these materials, their methods certainly would have been significantly different. In those days, safety precautions often were devised by trial and error; if inhaling a certain gas was found to make someone sick, the prescribed precaution was not to smell it. Today, since the physical and chemical properties of most known compounds are readily found in handbooks, proper care can be

TABLE 3.2

Disasters and Their Effects on Safety Measures

Type	Location and Date	Total Deaths	Safety Measures Enacted in Response to Disaster
Fire	City of Chicago, IL; October 9, 1871	250	Building codes prohibiting building structures; water reserve
Flood	Johnstown, PA; May 31, 1889	2209	Inspections required
Tidal wave	Galveston, TX; September 8, 1900	6000	Sea wall built
Fire	Iroquois Theatre, Chicago, IL; December 30, 1903	575	Stricter theater safety standards
Marine	<i>General Slocum</i> , burned in the East River, New York; June 15, 1904	1021	Stricter ship inspections; revision of statutes (life preservers, experienced crew, fire extinguishers)
Earthquake and fire	San Francisco, CA; April 18, 1906	452	Widened streets; limited heights of buildings; steel frame and fire resistant buildings
Mine	Monongah, WV; December 6, 1907	361	Creation of Federal Bureau of Mines; strengthened mine inspections
Fire	North Collinwood School, Cleveland, OH; March 8, 1908	176	Need realized for fire drills and planning of school structures
Fire	Triangle Shirt Waste Company, New York; March 25, 1911	145	Strengthening of laws concerning alarm signals, sprinklers, fire escapes, fire drills
Marine	<i>Titanic</i> struck iceberg, Atlantic Ocean; April 15, 1912	1517	Regulation regarding number of lifeboats; all passenger ships equipped for around the clock radio watch; International Ice Patrol
Explosion	New London School, TX; March 18, 1937	294	Odorants injected into natural gas
Fire	"Coconut Grove," Boston, MA; November 28, 1942	492	Ordinances regarding aisle space, electrical wiring, flame proofing of decorations, overcrowding; signs indicating maximum number of occupants; administration of blood plasma to prevent shock and the use of penicillin
Plane	Two-plane air collision over Grand Canyon, AZ; June 30, 1956	128	Controlled airspace expanded; use of infrared as a warning indicator

Source: Thygeson, A., *Accidents and Disasters: Causes and Countermeasures*, Prentice-Hall, Upper Saddle River, NJ, 1977. With permission.

exercised when working with these chemicals [24]. Labs are equipped with exhaust hoods and fans to minimize a buildup of gases. In addition, safety glasses and eyewash stations are required, and gloves and smocks are often required.

Many natural disasters are now accurately predicted, buying precious time in which warnings can be made and possible evacuation plans implemented. Radar equipment commonly track storms, and seismographs detect slight rumblings in the earth, which can provide early warning of potential earthquakes. Volcanic eruptions can be predicted by using seismic event monitors and aerial scanning of anomalies detected in the infrared region. Where natural disasters often occurred unexpectedly in the past, similar occurrences today are more predictable. Thus, there is more time for preparation and less likelihood of loss of life.

The use of computers and modern instrumentation has greatly enhanced plant safety. System overloads, uncontrollable reactions, and unusual changes (excursions) in temperature or pressure can be detected, with the information being relayed to a computer. The computer can then shut down the system or take the steps necessary to minimize the danger. Industry has come a long way from sniffing and tasting its way to safety.

It is anticipated that further safety advances will occur in the following five areas:

1. Development of inherently safer processes
2. Development of monitoring/detection devices that are more durable, cost-effective, reliable, and accurate
3. Development of new and improved secondary/backup containment systems
4. Development of more reliable "continuous" containment systems
5. Development of more reliable "discontinuous" containment systems

Illustrative Example 3.12

With reference to Section 3.5, describe the difference between *continuous* containment/treatment systems and *discontinuous* ones.

Solution

1. *Continuous* containment/treatment systems are required for health problems that exist on a round the clock, 24-7, day-to-day basis. In effect, it could be viewed as systems to manage "chronic" exposure situations.
2. *Discontinuous* containment/treatment systems are required for accidents that are severe but of a short duration. In effect, it could be viewed as systems to manage "acute" exposure situations.
3. The differences between these two processes and hazard systems are discussed in detail in Parts II and III.

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4

Health Risk versus Hazard Risk

4.1 Introduction

People face all kinds of risks every day, some voluntarily and others involuntarily. Therefore, risk plays a very important role in today's world. Studies on cancer caused a turning point in the world of risk because it opened the eyes of risk engineers, scientists, and health professionals to the world of risk assessments.

Both health risk assessments (HRAs) and hazard risk assessment (HZRA) are ultimately concerned with characterizing risk. As noted earlier, the description of risk is closely related to probability. For example, a probability of unity, i.e., 1.0, indicates that a health/hazard problem *will* occur; alternately, a probability of zero, i.e., 0.0, indicates that a health/hazard problem definitely will *not* occur.

Unfortunately, the word risk has come to mean different things to different people. Although defined earlier, here are two additional definitions. Webster [1] defines risk as "... the chance of injury, danger or loss ... to expose to the chance of injury, damage, or loss." Stander and Theodore [2] have defined it as "a combination of uncertainty and change." To compound this problem, there are *two* types of risk that environmental professionals are concerned with: *health risk* and *hazard risk*. However, these two classes of risk have been used interchangeably by practitioners, researchers, and regulators. Because of this confusion, one of the main objectives of this chapter is to both define and clarify the differences between these two risks.

Irrespective of the category of the applicable risks for a system, the total risk (see also Chapter 1), R_T , is given by the summation of the risk from all n events/scenarios, i.e.,

$$R_T = \sum_{i=1}^n R_i \quad (4.1)$$

In addition, the magnitude of each risk can be noted relative to the total risk.

Regarding human health risk, concern arises because chemicals can possibly elude natural defense mechanisms upon entering the human body. Exposure to chemicals can lead to various pathways of entry into the human body. These include inhalation, skin absorption (absorption), and ingestion (digestion system). It is fair to say that the dominant route of human exposure to hazardous chemicals is via inhalation. Note also that two types of potential exposures exist relative to the concentration and duration of the exposure. These are as follows:

1. *Chronic*: Continuous exposure occurring over long periods of time, generally months to years, at relatively low contaminant concentrations. Direct skin contact by immersion, splash, or contaminated air at chronic exposure levels involves contact with substances exhibiting low dermal activity.
2. *Acute*: Exposures that occur for relatively short periods of time, generally minutes to 1–2 days, at high exposure concentrations. In addition to inhalation, high concentrations of airborne substances might directly contact the skin, or liquids and sludges may be splashed onto the skin or into the eyes, leading to acutely toxic effects.

Alternatively, hazard risk, which is classified in the *acute* category, is described as (1) a ratio of hazards (e.g., an explosion) to failures of safeguards; (2) a triplet combination of event, probability, and consequences; or even (3) a measure of economic loss or human injury in terms of both an incident likelihood and the magnitude of the loss or injury.

Health risk and its assessments are addressed, in part, under the Clean Air Act (CAA) Section 112(d) and (f), where “EPA must promulgate (along with methods of calculating) residual risk standards for the source category as necessary to provide an ample margin of safety to protect public health.” Regarding hazard risk, the CAA’s Section 112(r), the *Risk Management Program* (RMP) rule (40 CFR Part 68), is designed to reduce the risk of accidental releases of acutely toxic, flammable, and explosive substances. Both of these risk terms are addressed in this chapter and the next chapter.

Six topics are addressed in the sections that follow:

- Introduction to the health risk assessment process
- Introduction to the hazard risk assessment process
- Qualitative risk assessment
- What are the differences?
- Uncertainty factors
- Future trends in environmental risk assessment

4.2 Introduction to the Health Risk Assessment Process

HRA provides an orderly, explicit, and consistent way to deal with scientific issues in evaluating whether a health problem exists and what the magnitude of the problem may be. This evaluation typically involves large uncertainties because the available scientific data are limited, and the mechanisms for adverse health impacts or environmental damage are only imperfectly understood.

Most human or environmental health problems can be evaluated by dissecting the analysis into four parts: health problem identification, dose-response assessment, exposure assessment, and risk characterization (see Figure 4.1). This four-step framework has been widely adopted by U.S. federal and state agencies plus international organizations that assess and manage health and environmental issues [3–5].

Regarding *health problem identification*, a problem may be defined as a specific toxic agent or a set of conditions that have the potential to cause adverse effects to human health or the environment. For some perceived problem, the risk assessment might stop with the first step in the process, i.e., problem identification, if no adverse effect is identified or if an agency elects to take regulatory action without further analysis [6]. Problem identification involves an evaluation of various forms of information in order to identify different health concerns. Atmospheric air, indoor air, water, land, hazardous substances, and toxic pollutants are some of the environmental media or agents that could be identified in this step in the HRA process.

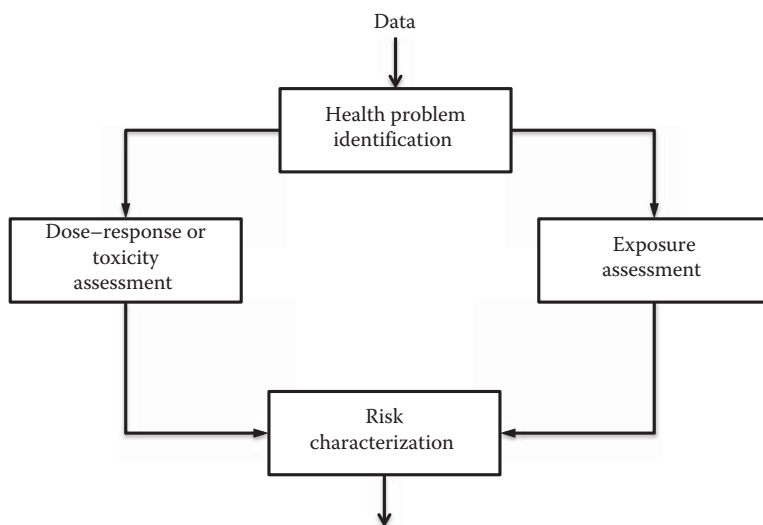


FIGURE 4.1
Health risk evaluation flowchart.

Dose–response or *toxicity assessment* is the next step required in an overall HRA. Responses/effects can be different since all chemicals and contaminants vary in their capacity to cause adverse effects. This step frequently requires that assumptions be made to relate experimental data for animals to humans. *Exposure assessment* is the determination of the magnitude, frequency, duration, and routes of exposure of human populations and ecosystems to hazardous agents. Finally, in *risk characterization*, the aforementioned toxicology and exposure data/information are combined to provide information on effects and obtain a qualitative or quantitative expression of health risk.

HRA thus involves the integration of information and analyses associated with the aforementioned four steps to provide a complete characterization of the nature and magnitude of risk and the degree of confidence associated with this characterization. A critical component of the assessment is the full elucidation of the uncertainties associated with each of the four major steps. All of the essential problems of toxicology are encompassed under this broad concept of risk assessment since it takes into account available dose–response data. It should treat uncertainty not by the application of arbitrary safety factors but by stating them in quantitatively and/or qualitatively explicit terms so that they are not hidden from decision makers. These four health risk evaluation steps receive detailed treatment in Chapters 7 through 11.

Illustrative Example 4.1

Certain assumptions are usually made about an “average” person’s attributes when applying HRAs to large groups of individuals. Describe these values.

Solution

The values normally employed for humans are as follows [7,8]:

1. Average body weight is 70 kg for an adult and 10 kg for a child.
2. The average daily drinking water intake is 2 L for an adult and 1 L for a child.
3. The average amount of air breathed per day is 20 m³ for an adult and 10 m³ for a child.
4. The average expected life span is 70 years.
5. The average dermal contact area is 1000 cm² for an adult and 300 cm² for a child.

4.3 Introduction to the Hazard Risk Assessment Process

As indicated earlier, many practitioners, researchers, and regulators have confused health risk with hazard risk and vice versa. Although both employ

a four-step method of analysis, the procedures are quite different, with each providing different results, information, and conclusions. Both do share a common concern in that they can negatively impact individuals, society, and the environment.

As with health risk, there is a serious lack of information on hazards and their associated implications. The unknowns in this risk area may be larger in number and greater in potential consequences than in the health risk area. It is the authors' judgment that hazard risks have unfortunately received something less than the attention they deserve. However, hazard risk analysis details are available and the traditional approaches successfully applied in the past are introduced in this section.

Much has been written about Michael Crichton's powerful science fiction thriller novel titled *Prey*. (The book was not only a best seller, but the movie rights were also sold for \$5 million.) In it, Crichton provides a frightening scenario in which swarms of nanorobots, equipped with special power generators and unique software, prey on living creatures. To compound the problem, the robots continue to reproduce without any known constraints. This scenario is an example of an accident and represents only one of a near-infinite number of potential hazards that can arise in any application. Although the probability of the horror scene portrayed by Crichton, as well as other similar hypothetical scenarios, is extremely low, steps and procedures need to be put into place to reduce, control, and hopefully eliminate low probability hazardous events from actually happening. This section attempts to provide some of this information.

Section 4.1 defined both "chronic" and "acute" problems. As indicated, when the two terms are applied to emissions, the former usually refers to ordinary, round-the-clock, everyday emissions, while the latter term deals with short, out-of-the-norm, accidental emissions. Thus, acute problems normally refer to accidents and/or hazards. The Crichton scenario discussed earlier is an example of an acute problem and one whose solution would be addressed/treated by an HZRA, rather than the health risk approach provided in the previous section.

There are several steps in evaluating the risk of an accident. These are detailed in Figure 4.2 and involve the following:

1. Any hazard in a system has to be identified; the event or series of events, e.g., a hazard problem, that can initiate an accident may also have to be identified [7–10].
2. The probability that the accident will occur also has to be determined.
3. The severity of the consequences of the accident must be determined.
4. The probability of the accident and the severity of its consequences are combined to characterize the hazard risk.

Additional details regarding the HZRA process are provided in Chapters 12 through 16.

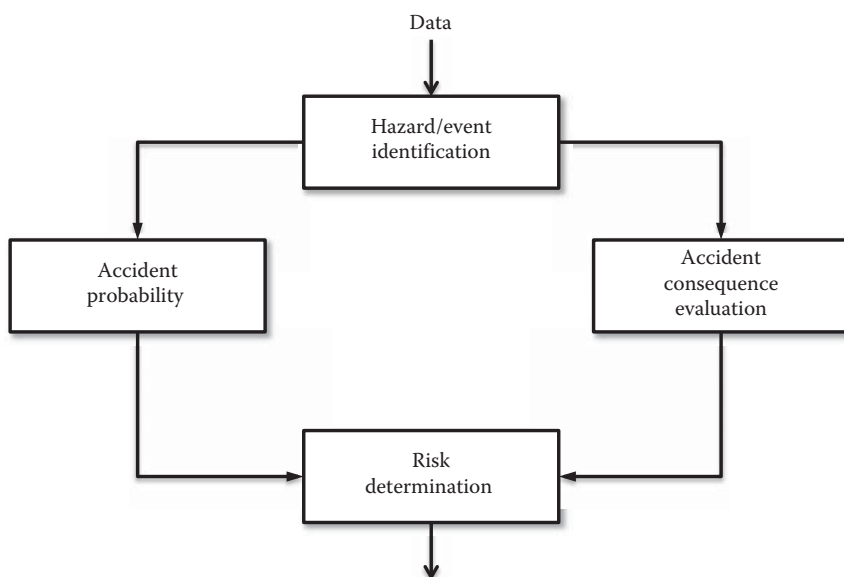


FIGURE 4.2
HZRA flowchart.

4.4 Qualitative Risk Scenarios

Numerous qualitative approaches to HRA and HZRA have been employed. One such qualitative risk categorization scheme that divides risk into various levels is provided in the following:

- Risk Level 1: Does not cause a problem
- Risk Level 2: Unlikely to cause a problem
- Risk Level 3: May cause a problem
- Risk Level 4: May cause a severe problem
- Risk Level 5: Will cause a severe problem

Risks may also be set in terms of a logarithmic scale of risk levels as seen in Table 4.1. These risk levels and ranges can apply on either an annual or a lifetime basis. Additional qualitative approaches to describing risk can be found in Chapter 11.

The reader should note that the aforementioned analysis and approach to describing potential health problems apply to health risks associated with chemicals. There are other classes of environmental health risks that do not pertain to chemicals. For example, health problems can arise

TABLE 4.1

Risk Level and Risk Range

Risk Level	Risk Range	
1	1 in 1 to 1 in 9	10^0 – 10^{-1}
2	1 in 10 to 1 in 99	10^{-1} – 10^{-2}
3	1 in 100 to 1 in 999	10^{-2} – 10^{-3}
4	1 in 1,000 to 1 in 9,999	10^{-3} – 10^{-4}
5	1 in 10,000 to 1 in 99,999	10^{-4} – 10^{-5}
6	1 in 100,000 to 1 in 999,999	10^{-5} – 10^{-6}
7	1 in 1,000,000 to 1 in 9,999,999	10^{-6} – 10^{-7}

immediately or soon after a hazard such as a hurricane or an earthquake, leaving local inhabitants without potable water for extended periods. This class of environmental health risk can be determined by replacing the steps of toxicity—exposure assessment pictured in Figure 4.1 with the steps of the probability of occurrence—consequence(s). The calculational approach then becomes similar to that provided in Figure 4.2 for HZRA problems. This point will be noted repeatedly throughout the chapter.

Illustrative Example 4.2

Does probability play a role in the characterization of risk for both health problems and hazards?

Solution

An integral part of describing risk is probability. Therefore, it plays a role in both HRA and HZRA. The role probability plays in HZRA is more apparent, as explicitly seen in Figure 4.2.

Illustrative Example 4.3

Is exposure to dioxins a health problem or a hazard problem?

Solution

It depends. If it is a continuous emission/exposure over an extended period of time at a low but chronically toxic concentration, it is a health problem, as defined in this chapter. If there is a massive release/exposure for a short duration but at a very high (acutely toxic) concentration, it is a hazard problem, as defined in this chapter.

Illustrative Example 4.4

Qualitatively describe Risk Level 6 in Table 4.1.

Solution

A Level 6 risk indicates that the risk associated with a health problem or a hazard problem is in the 1 in a 100,000 to 1 in a million range or the 10^{-5} to 10^{-6} range. This is often the maximum acceptable limit of annual risk for many environmental problems.

4.5 What Are the Differences?

The differences between HRA and HZRA can qualitatively be explained in terms of the words health and hazard. As noted earlier, health problems are generally of a chronic nature and related to the general state of well-being. Hazard problems are generally of an acute nature and relate to accidents that can be immediately harmful, immediately produce unhealthy results, or both.

The difference between HRA and HZRA is also demonstrated in Figures 4.1 and 4.2. Although both assessment processes involve a four-step procedure, the middle steps, that is, Steps 2 and 3, differ. Consider Step 2: For an HRA, this step is concerned with toxicology and ultimately requires information of a dose–response nature for the health problem in question. For an HZRA, this step is concerned with probability and requires information on the probability of the hazard problem occurring. Also consider Step 3: For an HRA, this step is concerned with exposure and ultimately demands information on a receptor’s degree of exposure for the health problem in question. For an HZRA, Step 3 involves determining the consequence of the hazard problem being evaluated.

Combining the data/information/calculations generated in Steps 2 and 3 provides risk results for either the HRA or HZRA. The HRA is obviously concerned with a health problem, while the HZRA is concerned with a hazard problem.

The differences can also be illustrated via simple examples. Suppose the following is provided for an HRA:

The health problem identification: ethylene oxide, EtO

Toxicology: concentration in excess of a given value produces death

Exposure: number of individuals’ exposure to above concentration

Risk: number of exposed individuals who will die

If 10 people are exposed to EtO from a population of 1 million, i.e., 10^6 , the risk to the *population* is 10×10^{-6} or 10^{-5} . If this information and results are based on what can occur on an annual basis, then the risk is also based on an annual basis.

Suppose the following is provided for an HZRA:

Hazard problem (event) identification: a biological attack on NYC by terrorists

Probability (of occurrence): one in a million, that is, 10^{-6}

Consequences (of attack): 1 million people will die, that is, 10^6

Assuming the probability is provided on an *annual* basis, the annual risk from this hazard is then calculated to be $(10^{-6})(10^6) = 10^0 = 1$. This indicates that the individual risk to the 10×10^6 New York metropolitan area residents is $1.0/10 \times 10^6$ or 10^{-7} or 0.1×10^{-6} on an *annual* basis.

One may therefore conclude that both HRA and HZRA provide risk information and numbers but they are related/associated with different problem categories. More detailed health risk and hazard risk calculations are provided in Chapters 11 and 16, respectively. Case studies for each, as well as a combination of both risk categories, can be found in Part IV.

4.6 Uncertainty Factors

Well, what about uncertainty? Qualitatively, uncertainty may be viewed as having two components: variability and lack of knowledge. The uncertainty factor associated with health risk and hazard risk result calculations will receive treatment throughout the book. This abbreviated section is intended to provide the reader with an introduction to *uncertainty* and better prepare the reader for the more detailed material to follow.

Uncertainty, whether applied to toxicological values, probability, consequences, risks, etc., may be described qualitatively or quantitatively. Qualitatively, descriptions include large, huge, monstrous, tiny, very small, etc. Quantitative terms describing the uncertainty associated with a value x are normally in the form $x \pm u$, where u provides a measure of the uncertainty (e.g., standard deviation, 95% confidence limit, etc., for mean of replicate measurements).

A substantial amount of information on uncertainty and uncertainty analysis is available. Useful references abound but, in general, there are three main sources of uncertainty that have been earmarked by practicing engineers and scientists:

1. Model uncertainty
2. Data uncertainty
3. General quality uncertainty

Model uncertainty reflects the weaknesses, deficiencies, and inadequacies present in any model and may be viewed as a measure of the displacement

of the model from reality. *Data uncertainty* results from incomplete data measurement, estimation, inference, or supposed expert opinion. *General quality uncertainty* arises because the practitioner often cannot identify every health problem or hazard incident. Naturally, the risk engineer's objective is to be certain that the major contributors to the risk are identified, addressed, and quantified. Uncertainty here arises from not knowing the individual risk contributions from those risk problems that have been omitted; one, therefore, may not be able to accurately predict the overall (or combined) risk. Byrd and Cothorn [11] have expanded this three-part uncertainty categorization in the following manner:

1. Subjective judgment
2. Linguistic imprecision
3. Statistical variation
4. Sampling error
5. Inherent randomness
6. Mathematical modeling
7. Causality
8. Lack of data or information
9. Problem formulation

Sensitivity and *importance* are also issues in the utilization of risk results. As noted earlier, uncertainty analysis is used to estimate the effect of data and model uncertainties on the risk estimate. Sensitivity analysis estimates the effect on calculated outcomes of varying inputs to the models individually or in combination. Importance analysis quantifies and ranks risk estimate contributions from subsystems or components of the complete system (e.g., individual incidents, groups of incidents, sections of a process, etc.)

To summarize, different assumptions can change any quantitative risk characterization by several orders of magnitude. The uncertainty that arises is related to how well (and often, consistently) input data are obtained, generated, or measured, and the degree to which judgment is involved in developing risk scenarios and selecting input data. Simply put by some, uncertainty arises from how data/evidence was both measured and interpreted. Despite these limitations and uncertainties, risk characterizations provide the practitioner with some assessment capabilities.

4.7 Future Trends in Environmental Risk Assessment

For the most part, future trends in environmental risk assessment will be found in hazard accident prevention, not hazard analysis. To help promote

hazard accident prevention, companies should start or expand employee-training programs. These programs should be designed to alert staff and employees about the hazards they are exposed to on the job. Training should also cover company safety policies and the proper procedures to follow in case an accident does occur. A major avenue to reducing risk will involve source reduction of hazardous materials [12]. Hazard risk education at the academic level is another area that will need improvement.

Communicating health risk and hazard risk has emerged as a major area of concern. Understanding risk communication dynamics is essential to successful risk communication efforts. Two-way communication with stakeholders (regulatory agencies, local residents, employees, etc.) prevents costly rework and permit delays and provides information useful for prioritizing risk management efforts. As communities have become more interested and concerned about environmental issues in recent years, the role of the environmental manager has expanded to include communications with key audiences. This interest and concern is certain to expand in the future. In addition to addressing the technical aspects of environmental health and hazard risks, efforts to address process, health, and lifestyle concerns have become more critical to the success of environmental projects and risk management.

Additional information is provided in Section 3.5 in the previous chapter.

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5

Environmental Regulatory Framework

5.1 Introduction

It is now 1970, a cornerstone year for modern environmental policy. The National Environmental Policy Act (NEPA), enacted on January 1, 1970, was considered a “political anomaly” by some. The NEPA was not based on specific legislation; instead, it referred in a general manner to environmental and quality-of-life concerns. The Council for Environmental Quality (CEQ), established by the NEPA, was one of the councils mandated to implement legislation. April 22, 1970, brought Earth Day, where thousands of demonstrators gathered all around the nation. The NEPA and Earth Day were the beginning of a long, seemingly never-ending debate over environmental issues [1].

The Nixon administration at that time became preoccupied with not only trying to pass more extensive environmental legislation but also implementing the laws. Nixon’s White House Commission on Executive Reorganization proposed, in the Reorganizational Plan #3 of 1970, that a single, independent agency be established, separate from the CEQ. The plan was sent to Congress by President Nixon on July 9, 1970, and this new U.S. Environmental Protection Agency (EPA) began operation on December 2, 1970. The EPA was officially born.

In many ways, the EPA is the most far-reaching regulatory agency in the federal government because its authority is so broad. The EPA is charged with protecting the nation’s land, air, and water systems. Under a mandate of national environmental laws, the EPA strives to formulate and implement actions that lead to a compatible balance between human activities and the ability of natural systems to support and nurture life [2].

The EPA works with the states and local governments to develop and implement comprehensive environmental programs. Federal laws such as the Clean Air Act (CAA); the Safe Drinking Water Act (SDWA); the Resource Conservation and Recovery Act (RCRA); and the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA), etc., all mandate involvement by state and local government in the details of implementation.

This chapter provides an overview of key environmental protection laws and subsequent regulations that affect the environment in the United States, particularly from a risk perspective. The following topics are addressed in this chapter:

- Review of the regulatory system
- Laws and regulations: the differences
- Role of the states
- Resource Conservation and Recovery Act
- Major toxic chemical laws administered by the U.S. EPA
- Legislative tools for controlling water pollution
- Superfund Amendments and Reauthorization Act of 1986
- Clean Air Act
- Occupational Safety and Health Act
- EPA's Risk Management Program
- Pollution Prevention Act of 1990

5.2 Regulatory System

Over the past four decades, environmental regulation has become a system in which laws, regulations, and guidelines have become interrelated. The history and development of this regulatory system has led to laws that focus principally on only one environmental medium independently at a time, i.e., air, water, or land. Some environmental managers feel that more needs to be done to manage all of the media simultaneously and in an integrated way. Hopefully, the environmental regulatory system will evolve into a truly integrated, multimedia management framework in the future.

Federal laws are the product of Congress. Regulations written to implement the laws are promulgated by the Executive Branch of government, but until judicial decisions are made regarding the interpretations of the regulations, there may be uncertainty about what regulations mean in real situations. Until recently, environmental protection groups were most frequently the plaintiffs in cases brought to court seeking interpretation of the law. Today, industry has become more active in this role.

Enforcement approaches for environmental regulations are environmental management oriented in that they seek to remedy environmental harm, not simply a specific infraction of a given regulation. All laws in a legal system may be used in enforcement to prevent damage or threats of damage to the environment or human health and safety. Tax laws (e.g., tax incentives) and

business regulatory laws (e.g., product claims and liability disclosures) are examples of laws not directly focused on environmental protection, but that may also be used to encourage compliance and discourage noncompliance with environmental regulations.

Common law also plays an important role in environmental management. Common law is the set of rules and principles relating to the government and security of persons and property. Common law authority is derived from the usages and customs that are recognized and enforced by the courts. In general, no infraction of the law is necessary when establishing a common law court action. A common law “civil wrong” (e.g., environmental pollution) that is brought to court is called a *tort*. Environmental torts may arise because of nuisance, trespass, or negligence.

Laws tend to be general and contain uncertainties relative to the implementation of principles and concepts they contain. Regulations derived from laws may be more specific but are also frequently too broad to allow clear translation into environmental technology practice. Permits are used to bridge this gap and prescribe specific technical requirements concerning the discharge of pollutants or other activities carried out by a facility that may impact the environment.

Most major federal environmental laws provide for citizen lawsuits. This empowers individuals to seek compliance or monetary penalties when these laws are violated and regulatory agencies do not take enforcement action against the violator.

Environmental regulations often come into being following the occurrence of a serious environmental health and/or hazard problem. Many are instituted to reduce or eliminate risk associated with these problems. However, costs are almost always incurred in these attempts to reduce/eliminate health and hazard problems, and the cost per level of risk reduction, e.g., dollars/lives saved, can be astronomical. Have standard cost-benefit analyses been applied in setting regulations? Unfortunately, primarily due to politics and the emotional complications of assigning a monetary value to a life saved, the answer is no.

Note: Regarding risk, EPA’s definition of how risk is used to develop regulations can be found in part of a preamble to a proposed regulation in 2008 at the following URL: <http://www.epa.gov/atw/degree/fr200008.pdf>

Illustrative Example 5.1

Define English common law.

Solution

Under English common law, the courts rely on *precedent*, i.e., earlier relevant and applicable judicial decisions. Interestingly, the Napoleonic Code is based on present-day rules, laws, and regulations.

Illustrative Example 5.2

Discuss the nature and purpose(s) of licenses and permits.

Solution

Both can be issued by local, state, and federal authorities/governments for the purpose of engaging in some sort of activity, usually of a business nature. It should be noted that a license or a permit is not an individual's right; it is simply a right provided by government to apply for such a license or permit. There is no legal requirement that such licenses or permits will be granted.

Illustrative Example 5.3

The term *liability* is closely tied to risk. In concise language, define the various liability terms. Explain how one's interpretation of liability affects financial analysis concerns associated with risk.

Solution

Liability implies responsibility for an action. An individual (or other entity) may be held liable for a result if, in the mind of the normal, prudent person, the individual failed to exercise due caution. Societal examples of failure to exercise due caution include driving too fast, losing control of a car, and causing damage to property or persons.

Strict liability implies responsibility without regard to prudence or care, that is, without regard to negligence. Such standards are imposed for a variety of activities, such as handling dynamite, statutory rape, or managing hazardous waste management. These standards require that proper caution be exercised at all times. Defenses available, if harm results, are limited.

Joint and several liability is an assignment of responsibility when two or more persons fail to exercise the proper care and a division of harm is not possible. If two hunters fire their weapons and a person is killed, and there is no way to determine which projectile caused the harm, both hunters may be each held liable for the harm to the aggrieved party. In the case of joint and several strict liability, each party who managed a waste may be responsible for any health risk caused by the waste. For example, the generator, the transporter, the storage facility, and an incinerator operator may each individually or collectively be responsible for risks caused by mismanagement during the treatment of a waste.

These provisions provide a tremendous impetus to industry to carefully address risk issues. This concept of liability also burdens industry with the threat of future costs as a result of someone else's improper actions. These values follow directly from this nation's system of government, which was created to assure that individual citizens do not suffer loss of property and freedoms (health) by the actions of others.

5.3 Laws and Regulations: The Differences

The following is a listing of some of the major differences between a federal *law* and a federal *regulation*:

1. A law (or act) is passed by both houses of Congress and signed by the president. A regulation is issued by a government agency such as the U.S. EPA or the Occupational Safety and Health Administration (OSHA).
2. Congress can pass a law on any subject it chooses. It is only limited by the restrictions in the constitution. A law can be challenged in court only if it violates the constitution. It may not be challenged if it is merely unwise, unreasonable, or even silly. If, for example, a law were passed that placed a tax on burping, it could not be challenged in court just because it was unenforceable. A regulation can be issued by an agency only if the agency is authorized to do so by the law passed by Congress. When Congress passes a law, it usually assigns an administrative agency to implement that law. A law regarding radio stations, for example, may be assigned to the Federal Communications Commission (FCC). Sometimes a new agency is established to implement a law. This was the case with the Consumer Product Safety Commission (CPSC). The OSHA is authorized by the Occupational Safety and Health Act to issue regulations that protect workers from exposure to the (hazardous) chemicals used in manufacturing processes.
3. Laws include a Congressional mandate directing the EPA, for example, to develop a comprehensive set of regulations. Regulations, or rulemakings, are issued by an agency, such as the EPA, that translates the general mandate of a statute into a set of requirements for the agency and the regulated community to follow.
4. Regulations are developed by an agency such as the EPA in an open and public manner according to an established process. When a regulation is formally proposed, it is published in an official government document called the *Federal Register* to notify the public of the agency's intent to create new regulations or modify existing ones. The EPA, for example, provides the public, which includes the potentially regulated community, with an opportunity to submit comments. Following an established comment period, the EPA may revise the proposed rule based on both an internal review process and public comments it received.
5. The final regulation is published, or promulgated, in the *Federal Register*. Included with the regulation is a discussion of the agency's rationale for the regulatory approach, known as preamble language.

Final regulations are compiled annually and incorporated in the *Code of Federal Regulations* (CFR) according to a highly structured format based on the topic of the regulation. This latter process is called *codification*, and each CFR title corresponds to a different regulatory authority. For example, EPA's regulations are in Title 40 of the CFR. The codified RCRA regulations can be found in Title 40 of the CFR, Parts 240–282. These regulations are often cited as 40 CFR, with the part (e.g., 40 CFR Part 264), or the part and section (e.g., 40 CFR Section 264.10) listed afterward.

6. A regulation may be challenged in court on the basis that the issuing agency exceeded the mandate given to it by Congress. If the law requires the agency to consider costs versus benefits of their regulation, the regulation could be challenged in court on the basis that the cost/benefit analysis was not correctly or adequately done. If the OSHA issues a regulation limiting a worker's exposure to a (hazardous) chemical to 1 part per million (ppm), OSHA could be called upon to prove in court that such a low limit was needed to prevent a worker from being harmed. Failure to prove this would mean that the OSHA exceeded its mandate under the law, as the OSHA is charged to develop standards only as stringent as those required to protect worker health and provide worker safety.
7. Laws are usually brief and general. Regulations are usually lengthy and detailed. The Hazardous Materials Transportation Act, for example, is approximately 20 pages long. It speaks in general terms about the need to protect the public from the dangers associated with transporting hazardous chemicals and identifies the Department of Transportation (DOT) as the agency responsible for issuing regulations implementing the law. The regulations issued by the DOT are several thousand pages long and are very detailed, down to the exact size, shape, design, and color of the warning placards that must be used on trucks carrying any of the thousands of regulated chemicals.
8. Generally, laws are passed infrequently. Often years pass between amendments to an existing law. For example, there has been very little recent activity in the environmental risk area. A completely new law on a given subject already addressed by an existing law is unusual. Laws are published as a "Public Law #____-____" and are eventually codified into the U.S. Code. Regulations are issued and amended frequently. Proposed and final new regulations and amendments to existing regulations are published daily in the Federal Register. Final regulations have the force of law when published.

5.4 Role of the States

The RCRA, like most federal environmental legislation, encourages states to develop and run their own programs as an alternative to EPA management. Thus, in a given state, the hazardous waste regulatory program may be run by the EPA or by a state agency. For a state to have jurisdiction over its hazardous waste program, it must receive approval from the EPA by showing that its program is at least as stringent as the EPA program.

States that are authorized to operate RCRA (or other similar) programs oversee the hazardous waste tracking system in their state, operate the permitting system for hazardous waste facilities, and act as the enforcement arm for the regulations in cases where an individual or a company practices illegal hazardous waste management. If needed, the EPA steps in to assist the states in enforcing the law. The EPA can also act directly to enforce the RCRA or other laws in states that do not yet have authorized programs. The EPA and the states currently act jointly to implement and enforce the regulations [3].

5.5 Resource Conservation and Recovery Act

Defining what constitutes a “hazardous waste” requires consideration of both legal and scientific factors. The basic definitions used in this chapter are derived from the RCRA of 1976, as amended in 1978, 1980, and 1986; the Hazardous and Solid Waste Amendments (HSWA) of 1984; and the CERCLA of 1980, as amended by the Superfund Amendments and Reauthorization Act (SARA) of 1986. A distinction exists between a hazardous waste and a hazardous substance within these statutory authorities. The former is regulated under the RCRA while the latter is regulated under the Superfund program.

Hazardous waste refers to “... a solid waste, or combination of solid wastes, which because of its quantity, concentration, or physical, chemical or infectious characteristics may [pose a] substantial present or potential hazard to human health or the environment when improperly ... managed ...” [RCRA, Section 1004(5)]. Under RCRA regulations, a waste is considered hazardous if it is reactive, ignitable, corrosive, or toxic or if the waste is listed as a hazardous waste in Title 40 Parts 261.31–33 of the *CFR* [4].

In addition to hazardous wastes defined under the RCRA, there are “hazardous substances” defined by Superfund. Superfund’s definition of a hazardous substance is broad and encompasses the lists of hazardous wastes or substances regulated under the Clean Water Act (CWA), the Clean Air Act

(CAA, the Toxic Substances Control Act (TSCA), and the RCRA. Essentially, Superfund considers a hazardous substance to be any hazardous substance or toxic pollutant identified under the CWA and applicable regulations, any hazardous air pollutant (HAP) listed under the CAA and applicable regulations, any imminently hazardous chemical for which a civil action has been brought under the TSCA, and any hazardous waste identified or listed under the RCRA and applicable regulations.

The RCRA of 1976 completely replaced the previous language of the Solid Waste Disposal Act of 1965 to address the enormous growth in the production of waste. The objectives of this act were to promote the protection of health and the environment and to conserve valuable materials and energy resources by [5,6]

1. Providing technical and financial assistance to state and local governments and interstate agencies for the development of solid waste management plans (including resource recovery and resource conservation systems) that promote improved solid waste management techniques (including more effective organizational arrangements), new and improved methods of collection, separation, and recovery of solid waste, and the environmentally safe disposal of nonrecoverable residues
2. Providing training grants in occupations involving the design, operation, and maintenance of solid waste disposal systems
3. Prohibiting future open dumping on the land and requiring the conversion of existing open dumps to facilities that do not pose a danger to the environment or to health
4. Regulating the treatment, storage, transportation, and disposal of hazardous wastes that have adverse effects on health and the environment
5. Providing for the promulgation of guidelines for solid waste collection, transport, separation, recovery, and disposal practices and systems
6. Promoting a national research and development program for improved solid waste management and resource conservation techniques; more effective organization arrangements; and new and improved methods of collection, separation, recovery, and recycling of solid wastes and environmentally safe disposal of nonrecoverable residues
7. Promoting the demonstration, construction, and application of solid waste management, resource recovery, and resource conservation systems that preserve and enhance the quality of air, water, and land resources
8. Establishing a cooperative effort among federal, state, and local governments and private enterprises in order to recover valuable materials and energy from solid waste

Structure-wise, the RCRA is divided into eight subtitles. These subtitles are (A) General Provisions; (B) Office of Solid Waste; Authorities of the Administrator; (C) Hazardous Waste Management; (D) State or Regional Solid Waste Plans; (E) Duties of the Secretary of Commerce in Resource Recovery; (F) Federal Responsibilities; (G) Miscellaneous Provisions; and (H) Research, Development, Demonstration, and Information. Subtitles C and D generate the framework for regulatory control programs for the management of hazardous and solid nonhazardous wastes, respectively. The hazardous waste program outlined under Subtitle C is the one most people associate with the RCRA [6].

Illustrative Example 5.4

List the major objectives of the RCRA.

Solution

As the major objectives of the RCRA, the act

1. Establishes a system under the EPA for identifying and controlling hazardous wastes from “cradle to grave,” i.e., from the point of generation through transport, treatment, storage, and final disposal
2. Develops guidelines under the EPA for acceptable solid waste management practices and preparation of state and regional solid waste management plans
3. Eliminates all open dumping and develops disposal prohibitions for certain wastes and liquids
4. Develops and implements resource conservation and resource techniques
5. Establishes exposure assessments for surface impoundments and landfills that address exposure resulting from releases from a facility or from transportation accidents

5.6 Major Toxic Chemical Laws Administered by the U.S. EPA

People have long recognized that sulfuric acid, arsenic compounds, and other chemical substances can cause fires, explosions, or poisoning. More recently, researchers have determined that many chemical substances such as benzene and a number of chlorinated hydrocarbons may cause cancer, birth defects, and other long-term health impacts. Today, the hazards of newly developed substances, including genetically engineered microorganisms and nanoparticles, are being evaluated. The EPA has a number of legislative tools to use for controlling the risks from these toxic substances (see Table 5.1).

TABLE 5.1

Major Toxic Chemical Laws Administered by the EPA

Statute	Provisions
Toxic Substances Control Act (TSCA)	Requires that the EPA be notified of any new chemical prior to its manufacture and authorizes EPA to regulate production, use, or disposal of a chemical
Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA)	Authorizes the EPA to register all pesticides, specify the terms and conditions of their use, and remove unreasonably hazardous pesticides from the marketplace
Federal Food, Drug, and Cosmetic Act	Authorizes the EPA, in cooperation with the FDA, to establish tolerance levels for pesticide residues in food and food products
Resource Conservation and Recovery Act (RCRA)	Authorizes the EPA to identify hazardous wastes and regulate their generation, transportation, treatment, storage, and disposal
Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA)	Requires the EPA to designate hazardous substances that can present substantial danger to human health and the environment and authorizes the cleanup of sites contaminated with such substances
Clean Air Act (CAA)	Authorizes the EPA to set emission standards to limit the release of HAPs
Clean Water Act (CWA)	Requires the EPA to establish a list of toxic water pollutants and set standards for them in wastewater discharges
Safe Drinking Water Act (SDWA)	Requires the EPA to set drinking water standards to protect public health from hazardous substances
Marine Protection, Research, and Sanctuaries Act (MPRSA)	Regulates ocean dumping of toxic contaminants
Asbestos School Hazard Act (ASHA)	Authorizes the EPA to provide loans and grants to schools with financial need for abatement of severe asbestos hazards
Asbestos Hazard Emergency Response Act (AHERA)	Requires the EPA to establish a comprehensive regulatory framework for controlling asbestos hazards in schools
Emergency Planning and Community Right-to-Know Act (EPCRA)	Requires states to develop programs for responding to hazardous chemical releases, and requires industries to report on the presence and release of certain hazardous substances

The Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA) of 1972 regulates all pesticides used in the United States. When first enacted in 1947, the FIFRA was administered by the U.S. Department of Agriculture and was intended to protect consumers against fraudulent pesticide products. When many pesticides were registered, their potential for causing health and environmental problems was unknown. In 1970, the EPA assumed responsibility for the FIFRA, which was amended in 1972 to shift emphasis to health and environmental protection. Allowable levels of pesticides in food are specified under the authority of the Federal Food, Drug, and Cosmetic Act (FFDCA) of 1954. Today, the FIFRA contains registration and labeling requirements

for pesticide products. The EPA must approve any use of a pesticide, and manufacturers must clearly state the conditions of that use on the pesticide label. Some pesticides are also listed as hazardous wastes and are subject to RCRA rules when discarded.

The TSCA authorizes the EPA to control the risks that may be posed by the thousands of commercial chemical substances and mixtures (chemicals) that are not regulated as drugs, food additives, cosmetics, or pesticides. Under the TSCA, the EPA can, among other things, regulate the manufacture and use of a chemical substance and require testing for cancer and other effects these substances cause to humans and the environment. The TSCA regulates the production and distribution of new chemicals and governs the manufacture, processing, distribution, and use of existing chemicals. Among the chemicals controlled by TSCA regulations are polychlorinated biphenyls (PCBs), chlorofluorocarbons, and asbestos. In specific cases, there is an interface with RCRA regulations. For example, PCB disposal is generally regulated by the TSCA. However, hazardous wastes mixed with PCBs are regulated under the RCRA. Under both the TSCA and the FIFRA, the EPA is responsible for regulating certain biotechnology products, such as genetically engineered microorganisms designed to control pests or as components of an industrial processes.

The CAA, in Section 112, listed 189 air pollutants. The CAA also requires emission standards for many types of air emission sources, including RCRA-regulated incinerators and industrial boilers or furnaces.

The CWA lists substances to be regulated by effluent limitations in 21 primary industries. The CWA substances are incorporated into both the RCRA and the CERCLA. In addition, the CWA regulates discharges from publicly owned treatment works (POTWs) to surface waters and industrial discharges to POTWs (through the pretreatment program). Some hazardous wastewaters that would generally be considered RCRA-regulated wastes are covered under the CWA through the National Pollutant Discharge Elimination System (NPDES) permit program to dispose of these wastewaters, as the CWA is given authority over treatment tanks. Sludges from these tanks, however, are subject to RCRA regulations when they are removed.

The SDWA regulates underground injection, including deep-well injection systems. Prior to underground injection, a permit must be obtained that imposes conditions that must be met to prevent the endangerment of underground sources of drinking water.

The Marine Protection, Research, and Sanctuaries Act (MPRSA) of 1972 regulates the transportation of material destined for ocean disposal and prevents the disposal of any material in oceans that could affect the marine environment. Amendments enacted in 1988 were designed to end ocean disposal of sewage sludge, industrial waste, and medical wastes [4].

Additional information on the management and regulation of toxic chemicals in the United States is available at the TSCA 8(e) website via <http://www.epa.gov/oppt/chemtest/pubssect8e.htm>

Illustrative Example 5.5

Which of the following statements is *not* a definition of a “toxic substance”?

1. A substance that has an immediate or a long-term adverse effect on the environment
2. A substance that enters a living organism and metabolizes into its component derivatives
3. A substance constituting or that may constitute a danger to the environment on which human life depends
4. A substance constituting or that may constitute a danger in the United States to human life or to health

Solution

The answer is Statement 2. All of the others (1, 3, and 4) are correct definitions of a “toxic substance.”

Illustrative Example 5.6

What are the molecular and structural formulae for the following toxic air compounds?

1. Formaldehyde
2. Carbon tetrachloride

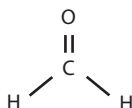
Solution

The molecular formulae for these compounds are as follows:

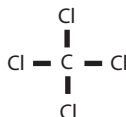
1. Formaldehyde: CH_2O
2. Carbon tetrachloride: CCl_4

The structural formulae for these compounds are as follows:

1. Formaldehyde:



2. Carbon tetrachloride:



5.7 Legislative Tools for Controlling Water Pollution

Congress has provided the EPA and the states with the three aforementioned primary statutes to control and reduce water pollution, i.e., the CWA, the SDWA, and the MPRSA. Each statute provides a variety of tools that can be used to meet the challenges and complexities of reducing water pollution in the nation, and each is discussed in some detail below.

5.7.1 Clean Water Act

Under the CWA, the states adopt water quality standards (WQSs) for every stream within their respective borders. These standards include a designated use such as fishing or swimming and prescribe criteria to protect that use. The criteria are pollutant specific and represent the permissible levels of substances in the waters that would enable the use to be achieved or maintained. WQSs are the basis for nearly all water quality management decisions. Depending upon the standard adopted for a particular stream, controls may be needed to reduce the pollutant levels. WQSs are reviewed every 3 years and revised as needed.

Under the CWA's *NPDES*, the discharge of pollutants into the waters of the United States is prohibited unless an NPDES permit is issued by the EPA or a state. These permits must be renewed at least once every 5 years. There are approximately 58,000 industrial and 15,000 municipal facilities that currently have NPDES permits. An NPDES permit contains effluent limitations plus monitoring and reporting requirements. Effluent limitations are restrictions on the amount of specific pollutants that a facility can discharge into a stream, river, or harbor. Monitoring and reporting requirements are specific instructions on how sampling of the effluent should be performed to check whether the effluent limitations are being met. Instructions include required sampling frequency (i.e., daily, weekly, or monthly) and the type of monitoring required. The permittee is required to regularly report the monitoring results to the EPA and state authorities. When a discharger fails to comply with the effluent limitations or monitoring and reporting requirements, the EPA or the state may take enforcement action against them to force them back into compliance.

Congress recognized that it would be an overwhelming task for the EPA to establish effluent limitations for each individual industrial and municipal discharger. Therefore, Congress authorized the agency to develop uniform effluent limitations for each category of point source (defined point of waste discharge to the environment, usually through a discharge pipe) such as steel mills, paper mills, and pesticide manufacturers. The EPA develops these effluent limitations on the basis of many factors, most notably available efficient treatment technologies. Once the EPA proposes an effluent limit and public comments are received, the EPA or the states issue NPDES permits

using the technology-based limits to all point sources within that industry category. Sewage treatment plants also are provided with effluent limitations based on technology performance.

These effluent limitations represent minimum treatment efficiency standards, but pollutant removal efficiencies that are more stringent than those based on effluent limits are often necessary to ensure that state-developed WQSs are met. For example, several different facilities may be discharging into one stream, creating pollutant levels harmful to fish. In this case, the facilities on that stream must meet more stringent treatment requirements, known as *Water Quality Based Limitations*, or *Stream Standards*. These stream standards are developed by determining the amount of each pollutant that the stream can safely assimilate and back calculating permit limits such that these levels in the stream from all dischargers are not exceeded [7]. This process of determining allowable waste discharges from individual facilities is called a *Waste Load Allocation* and is a part of the total maximum daily load (TMDL) process.

Strategies to address impaired waters must consist of a TMDL or another comprehensive approach that includes a functional equivalent of a TMDL. In essence, TMDLs are “pollutant budgets” for a specific water body or segment, which, if not exceeded, would result in attainment of WQSs.

The CWA requires that TMDLs be developed only for waters affected by pollutants where implementation of the technology-based controls imposed upon point sources by the CWA and EPA regulations would not result in achievement of WQSs. At this time, most point sources have been issued NPDES permits with technology-based discharge limits. In addition, a substantial fraction of point sources have more stringent water quality-based permit limits. But, because nonpoint sources (sources with an undefined point of waste discharge to the environment such as surface runoff from fields) are major contributors of pollutant loads to many water bodies, even these more stringent limits on point sources have not resulted in attainment of all WQSs.

The EPA and the U.S. Army Corps of Engineers jointly implement a permit program regulating the discharge of dredged or fill material into waters of the United States, including wetlands. As part of this program, the EPA’s principal responsibility, as set forth in the CWA, is to develop the substantive environmental criteria by which permit applications are evaluated. The EPA also reviews the permit applications and, if necessary, can nullify permits that would result in significant environmental damage.

The National Estuary Program is also regulated under the CWA. States nominate and the EPA selects estuaries of national significance that are threatened by pollution, development, or overuse. The EPA and the involved state(s) form a management committee consisting of numerous work groups to assess the problems, identify management solutions, and develop and oversee implementation of plans for addressing the problems.

See also U.S. EPA [7] for more information on the establishment and implementation of WQSs.

Illustrative Example 5.7

Describe in detail what WQSs are.

Solution

WQSs are aimed at translating the broad goals of the CWA into water body-specific objectives. Ideally, WQSs should be expressed in terms that allow quantifiable measurement. WQSs, like the CWA overall, apply only to the waters of the United States. As defined in the CWA, “waters of the United States” apply only to surface waters—rivers, lakes, estuaries, coastal waters, and wetlands. Not all surface waters are legally “waters of the United States.” Generally, however, those waters include the following:

1. All interstate waters
2. Intrastate waters used in interstate and/or foreign commerce
3. Tributaries of the above waters
4. Territorial seas at the cyclical high tide mark
5. Wetlands adjacent to all the aforementioned areas

The exact dividing line between “waters of the United States” according to the CWA and other waters can be hard to determine, especially with regard to smaller streams, ephemeral water bodies, and wetlands not adjacent to other “waters of the United States.” In fact, the delineation changes from time to time as new court rulings are handed down, new regulations are issued, or the act itself is modified.

Designated uses (DUs), water quality criteria (WQC), and an antidegradation policy constitute the three major components of WQSs program.

DUs of a water body are those uses that society, through various units of government, determines should be attained in the water body. The DUs are the goals set for the water body. In some cases, these uses have already been attained, but sometimes conditions in a water body do not support all the DUs.

WQC are descriptions of the conditions in a water body necessary to support the DUs. These can be expressed as concentrations of pollutants, temperature, pH, turbidity units, toxicity units, or other quantitative measures. WQC can also be narrative statements such as “no toxic chemicals in toxic amounts.”

Antidegradation policies are a component of state/tribal WQSs that establish a set of rules that should be followed when addressing proposed activities that could lower the quality of high-quality waters, i.e., those with water quality better than necessary to meet the DUs.

See also U.S. EPA, [7] for more information on the establishment and implementation of WQSs.

5.7.2 Safe Drinking Water Act

The EPA establishes standards for drinking water quality through the SDWA. These standards represent the maximum contaminant levels (MCLs) and consist of numerical criteria for specified contaminants. Local water supply systems are required to monitor their drinking water periodically for contaminants with MCLs and for a broad range of other contaminants as specified by the EPA. Additionally, to protect underground sources of drinking water, the EPA requires periodic monitoring of wells used for underground injection of hazardous waste, including monitoring of the ground water above the wells.

States have the primary responsibility for the enforcement of drinking water standards, monitoring, and reporting requirements. States also determine requirements for environmentally sound underground injection of wastes. The SDWA also authorizes the EPA to award grants to states for developing and implementing programs to protect drinking water at the tap and in groundwater resources. These grant programs may be for supporting state public water supplies, wellhead protection, and underground injection programs, including compliance and enforcement.

The CWA and the SDWA place great reliance on state and local initiatives in addressing drinking water and water quality problems. With the enactment of the 1986 SDWA Amendments and the 1987 Water Quality Act Amendments, significant additional responsibilities were assigned to the EPA and the states. Faced with many competing programs and limited resources, the public sector will need to set priorities. With this in mind, the EPA is encouraging states to address their water quality problems by developing State Clean Water Strategies. These strategies are to set forth state priorities over a multiyear period. They will help target the most valuable and/or most threatened water resources for protection.

Success in the water programs is increasingly tied to state and local leadership and decision making, and to public support. The EPA works with state and local agencies, industry, environmentalists, and the public to develop environmental agenda in the following three areas:

1. *Protection of drinking water.* Although more Americans are receiving safer drinking water than ever before, there are still serious problems with contamination of drinking water supplies and of groundwater that is or could be used for human consumption. Contaminated groundwater has caused well closings. The extent and significance of contamination by toxics has not been fully assessed for most of the nation's rivers and lakes, which are often used for drinking water supply. All of these issues are areas for continued work and improvement.
2. *Protection of critical aquatic habitat.* Contamination or destruction of previously underprotected areas such as oceans, wetlands, and near coastal waters must be addressed.

3. *Protection of surface water resources.* The EPA and the states will need to establish a new phase of the federal–state partnership in ensuring continuing progress in addressing conventional sources of pollution [8].

See also <http://www.epa.gov/safewater/sdwa/30th/factsheets/understand.html>, for more information regarding the SDWA and federal and state initiatives for water quality improvements.

Illustrative Example 5.8

Describe the process of setting drinking water standards.

Solution

The EPA sets primary drinking water standards through a three-step process. First, the EPA identifies contaminants that may adversely affect public health and that occur in drinking water with a frequency and at levels that pose a threat to public health. The EPA identifies these contaminants for further study and determines the contaminants to potentially regulate. Second, the EPA determines a maximum contaminant level goal (MCLG) for contaminants it decides to regulate. This goal is the level of a contaminant in drinking water below which there is no known or expected risk to health. These goals allow for a margin of safety. Third, the EPA specifies an MCL, the maximum permissible level of a contaminant in drinking water that is delivered to any user of a public water system that represents an acceptable health risk to the public. These levels are enforceable standards and are set as close to the goals as “feasible.”

The SDWA defines “feasible” as the level that may be achieved with the use of the best technology, treatment techniques, and other means that the EPA finds (after examination for efficiency under field conditions) are available, taking cost into consideration. When it is not economically or technically “feasible” to set a maximum level, or when there is no reliable or economic method to detect contaminants in the water, the EPA instead sets a required treatment technique that specifies a method to treat the water to remove contaminants.

Illustrative Example 5.9

Describe compliance enforcement provisions of the SDWA.

Solution

National drinking water standards are legally enforceable, which means that both the EPA and the states can take enforcement actions against water systems not meeting safety standards. The EPA and the states may issue administrative orders, take legal actions, or fine utilities. The EPA and the states also work to increase water system capacity and reliability.

5.7.3 Marine Protection, Research, and Sanctuaries Act (Title 1)

The EPA designates sites and times for ocean dumping. Actual dumping at these designated sites requires a permit. The EPA and the Corps of Engineers share this permitting authority, with the Corps responsible for the permitting of dredged material (subject to an EPA review role) and the EPA responsible for permitting all other types of materials. The Coast Guard monitors these waste disposal activities and the EPA is responsible for assessing penalties for violations.

5.8 Oil Pollution Act

The Oil Pollution Act (OPA) was signed into law in August 1990, largely in response to rising public concern following the *Exxon Valdez* incident. The OPA improved the nation's ability to prevent and respond to oil spills by establishing provisions that expand the federal government's ability and provide the money and resources necessary to respond to oil spills. The OPA also created the national Oil Spill Liability Trust Fund, which is available to provide up to \$1 billion per spill incident for response and remediation expenditures, along with \$500 million per spill incident for natural resource damage assessments and claims, which are cost recoverable from Principal Responsible Parties (PRPs). Costs for spill cleanup or natural resource damages exceeding these limits are potentially the liability of the federal and state governments. This fund replaced the fund established under the CWA and other oil pollution funds, and its current revenue sources include a 5 cent per barrel tax on U.S. produced and imported petroleum products, cost recovery from PRPs, fines and penalties levied against PRPs for violations of the law, and interest on the fund balance. The act mandates prompt and adequate compensation for those harmed by oil spills and an effective and consistent system of assigning liability. The act also strengthens requirements for the proper handling, storage, and transportation of oil and for a full and prompt response in the event oil discharges occur. The act does so in part by amending Section 311 of the CWA. There are eight titles codified under the act, details of which are available in the literature. Regulations to implement the oil pollution control act are found at 40 CFR 112.

In addition, the OPA provided new requirements for contingency planning both by government and industry. The National Oil and Hazardous Substances Pollution Contingency Plan (NCP) has been expanded in a three-tiered approach: the federal government is required to direct all public and private response efforts for certain types of spill events; Area Committees—composed of federal, state, and local government officials—must develop detailed, location-specific Area Contingency Plans; and owners or operators

of vessels and certain facilities that pose a serious threat to the environment must prepare their own Facility Response Plans.

Finally, the OPA increased penalties for regulatory noncompliance, broadened the response and enforcement authorities of the federal government, and preserved state authority to establish laws governing oil spill prevention and response.

The 2010 oil spill in the Gulf of Mexico, resulting from an explosion on BP's Deepwater Horizon drilling rig, caused far-reaching environmental ramifications, many of which will take a significant period of time to be fully realized. The situation is extremely complex, and it is fair to say that there will be an extended period of time for all the liability, regulatory issues, and responsibilities to be fully realized. This incident has prompted review by the Government Accounting Office (GAO) of the Oil Spill Liability Trust Fund as the fund balance as of September 30, 2010, was only \$1.69 billion, while BP has estimated cleanup costs and damage claim reimbursements to amount to tens of billions of dollars. In response to the release and a growing recognition of the magnitude of the environmental and economic damage it has caused, BP established a \$20 billion trust administered by the Gulf Coast Claims Facility, to reimburse recovery, remediation, and economic and natural resource damage claims justifiably attributed to the Deepwater Horizon incident. While BP has publicly stated they will pay for all costs associated with the Deepwater Horizon oil spill, even those exceeding the OPA statutory limits on their liability, there remains a large potential liability for the federal government that the GAO has recommended be carefully reviewed in case of future incidents of this magnitude [9].

At the time of the preparation of this chapter, the Administration indicated it would require significantly more environmental review before approving new offshore drilling permits. These reviews are part of a wave of new regulations and legislation that could fundamentally remake the industry. This could be a turning point for offshore oil exploration—similar to the Three Mile Island nuclear accident (see Chapter 4) that contributed to a virtual 30 year moratorium on nuclear power plant construction. The new permits for offshore rigs will, in effect, be subjected to increased environmental, safety, technical, and financial requirements.

Additional details on the OPA are available at <http://www.epa.gov/oilspill/opaover.htm>

5.9 Superfund Amendments and Reauthorization Act (SARA) of 1986

The 1986 Amendments to the CERCLA, known as the SARA, authorized \$8.5 billion for both the emergency response and longer term (or remedial)

cleanup programs for abandoned and uncontrolled hazardous waste sites. The SARA Amendments focused on

1. *Permanent remedies.* The EPA must implement permanent remedies to the maximum extent practicable. A range of treatment options are considered whenever practicable.
2. *Complying with other regulations.* Applicable or relevant and appropriate requirements (ARARs) from other federal, state, or tribal environmental laws must be met at Superfund sites where remedial actions are taken. In addition, state standards that are more stringent than federal standards must be met in cleaning up sites.
3. *Alternative treatment technologies.* Cost-effective treatment and recycling must be considered as an alternative to the land disposal of wastes. Under the RCRA, Congress banned land disposal of some wastes. Many Superfund site wastes, therefore, are banned from disposal on the land; alternative treatments are under development and should be used where possible.
4. *Public involvement.* Citizens living near Superfund sites are encouraged to become involved in the site decision-making process. They are also able to apply for technical assistance grants that further enhance their understanding of site conditions and activities.
5. *State involvement.* States and tribes are encouraged to participate actively as partners with the EPA in addressing Superfund sites. They assist in making the decisions at sites, can take responsibility in managing cleanups, and can play an important role in oversight of PRPs.
6. *Enforcement authorities.* Settlement policies were strengthened through Congressional approval and inclusion in SARA. Different settlement tools, such as *de minimis* settlements (settlements with PRPs that were minor contributors), are part of the act.
7. *Federal facility compliance.* Congress emphasized that federal facilities “are subject to, and must comply with, this act in the same manner and to the same extent ... as any non-government entity.” Mandatory schedules have been established for federal facilities to assess their sites, and if listed on the National Priority List (NPL), to clean up such sites. The EPA is assisting and overseeing federal agencies with these requirements.

These amendments expanded research and development, especially in the area of alternative technologies, and also provided for more training for state and federal personnel in emergency preparedness, disaster response, and hazard mitigation.

Major provisions of Title III of SARA (also known as Emergency Planning and Community Right-to-Know Act or EPCRA) include:

1. *Emergency planning.* EPCRA established a broad-based framework at the state and local levels to receive chemical information from manufacturers and use that information in communities for chemical emergency planning.
2. *Emergency release notification.* EPCRA requires facilities to report certain releases of extremely hazardous chemicals and hazardous substances to their state and local emergency planning and response officials.
3. *Hazardous chemical inventory reporting.* EPCRA requires facilities to maintain a material safety data sheet (MSDS) for each hazardous chemical stored or used in the work place and to submit those sheets to state and local authorities. It also requires them to submit an annual inventory report for those same chemicals to local emergency planning and fire protection officials, as well as state officials.
4. *Toxic release inventory (TRI) reporting.* EPCRA requires facilities to annually report on routine emissions of certain toxic chemicals to the air, land, or water. Facilities must report if they are in Standard Industrial Classification (SIC) Codes 20 through 39 (i.e., manufacturing facilities) with 10 or more employees and that manufacture or process any of 650 listed chemical compounds in amount greater than specified threshold quantities. If the chemical compounds are considered persistent, bioaccumulative, or toxic, the thresholds are much lower. The EPA is required to use these data to establish a national chemical release inventory database, making the information available to the public through computers, via telecommunications, and by other means.

This section also receives treatment in the next chapter. Additional details regarding Superfund, SARA, and EPCRA programs and requirements can be found at the following URL: <http://www.epa.gov/superfund/action/law/cercla.htm>

Illustrative Example 5.10

Describe the details of the SARA.

Solution

The SARA amended CERCLA on October 17, 1986. The SARA reflected EPA's experience in administering the complex Superfund program during its first 6 years and made several important changes and additions to the program. Specifically, the SARA

1. Stressed the importance of permanent remedies and innovative treatment technologies in cleaning up hazardous waste sites
2. Required Superfund actions to consider the standards and requirements found in other state and federal environmental laws and regulations

3. Provided new enforcement authorities and settlement tools
4. Increased state involvement in every phase of the Superfund program
5. Increased the focus on human health problems posed by hazardous waste sites
6. Encouraged greater citizen participation in making decisions on how sites should be cleaned up
7. Increased the size of the trust fund to \$8.5 billion

The SARA also required the EPA to revise the Hazard Ranking System (HRS) to ensure that it accurately assessed the relative degree of risk to human health and the environment posed by uncontrolled hazardous waste sites that may be placed on the NPL.

Additional details of the SARA program can be found at <http://www.epa.gov/superfund/action/law/sara.htm>

Illustrative Example 5.11

Outline an emergency response plan under SARA Title III.

Solution

The following information must be included in an emergency response plan:

1. The identification of facilities where a hazardous substance is present in an amount in excess of the threshold planning quantity and whether it is being produced, used, or stored
2. Transportation routes of hazardous substances to or from the facility and identification of facilities such as hospitals, natural gas facilities, etc., which may be in the proximity of the intended route
3. The methods and procedures to be followed by facility operators and local emergency and medical personnel in the event of the release of a hazardous substance
4. The designation of community and facility emergency coordinators who shall make the necessary determinations in implementing an emergency plan
5. The procedures providing reliable, effective, and timely notification by the facility emergency coordinator to persons designated in the emergency plan and to the public in the event that a release has occurred
6. The methods for determining the occurrence of a release and the area or population likely to be affected by such a release
7. A description of emergency equipment and facilities in the community and at each facility in the community that is subject to Title III requirements, as well as the identification of the persons responsible for such equipment and facilities
8. Evacuation plans that include provisions for a precautionary evacuation and alternative traffic routes

9. Training programs that include schedules for training of local emergency response and medical personnel as well as facility personnel

See the next chapter for additional details regarding emergency response planning under SARA Title III.

Illustrative Example 5.12

Compare and note the differences between a spill prevention control and countermeasure (SPCC) plan and the emergency response plan of Title III.

Solution

1. The major difference between the two plans is that the plan under Title III addresses all hazardous and toxic chemicals where the SPCC plan only addresses oil.
2. The SPCC plan considers the prediction, containment, and correction of a spill, whereas the emergency response plan under Title III specifies the sequence of actions to be followed once an emergency situation develops. It also defines the roles and functions of the emergency response team.

5.10 Clean Air Act

The Clean Air Act (CAA) defines the national policy for air pollution abatement and control in the United States. It establishes goals for protecting health and natural resources and delineates what is expected of federal, state, and local governments to achieve those goals. The CAA, which was initially enacted as the Air Pollution Control Act of 1955, has undergone several revisions over the years to meet the ever-changing needs and conditions of the nation's air quality. On November 15, 1990, the president signed the most recent amendments to the CAA, referred to as the 1990 Clean Air Act Amendments. Embodied in these amendments were several progressive and creative new themes deemed appropriate for effectively achieving air quality goals and for reforming the air quality control regulatory process. Specifically, the amendments

1. Encouraged the use of market-based principles and other innovative approaches similar to performance-based standards, plus emission banking and trading
2. Promoted the use of clean, low-sulfur coal and natural gas, as well as innovative technologies to clean high-sulfur coal through provisions in the Acid Rain Program

3. Reduced energy waste and created enough of a market for clean fuels derived from grain and natural gas to cut dependency on oil imports by 1 million barrels per day
4. Promoted energy conservation through provisions of the Acid Rain Program that gave utilities flexibility to obtain needed emission reductions through programs that encouraged customers to conserve energy

Several of the key provisions of the act are reviewed below.

5.10.1 Provisions for Attainment and Maintenance of National Ambient Air Quality Standards

Although the CAA brought about significant improvements in the nation's air quality, urban air pollution problems of ozone (smog), carbon monoxide (CO), and particulate matter (PM) persist. In 1995, approximately 70 million U.S. residents were still living in counties with ozone levels exceeding the EPA's current ozone standard.

The CAA, as amended in 1990, established a more balanced strategy for the nation to address the problem of urban smog. Overall, the amendments revealed the Congress's high expectations of the states and the federal government. While it gave states more time to meet air quality standards (up to 20 years for ozone in Los Angeles), it also required states to make constant progress in reducing emissions. It required the federal government to reduce emissions from cars, trucks, and buses; from consumer products such as hair spray and window-washing compounds; and from ships and barges during loading and unloading of petroleum products. The federal government also developed the technical guidance that states need to control stationary sources.

The CAA directly addresses urban air pollution problems of ozone (smog), CO, and PM. Specifically, it clarifies how areas are designated and redesignated "attainment." It also allows the EPA to define the boundaries of "nonattainment" areas, i.e., geographical areas whose air quality does not meet federal ambient air quality standards designed to protect public health. The law also establishes provisions defining when and how the federal government can impose sanctions on areas of the country that have not met certain conditions.

For the pollutant ozone, the CAA established nonattainment area classifications according to the severity of the area's air pollution levels. These classifications are marginal, moderate, serious, severe, and extreme. The EPA assigns each nonattainment area one of these categories, thus triggering varying requirements the area must comply with in order to meet the ozone standard.

These nonattainment areas have to implement different control measures, depending upon their classification. Marginal areas, e.g., are the closest to

meeting the standard. They are required to conduct an inventory of their ozone-causing emissions and institute a permit program. Nonattainment areas with more serious air quality problems must implement various control measures. The worse the air quality, the more controls these areas are mandated to implement.

5.10.2 Provisions Relating to Mobile Sources

While motor vehicles built today emit fewer pollutants than those built in the 1960s (60%–80% less, depending on the pollutant), cars and trucks still account for almost half the emissions of ozone precursors (volatile organic compounds [VOCs] and nitrogen oxides [NO_x]) and up to 90% of the CO emissions in urban areas. The principal reason for this problem is the rapid growth in the number of vehicles on the roadways and the increasing number of total miles each is driven. This growth has offset a large portion of the emission reductions gained from motor vehicle controls.

In view of the continuing growth in automobile emissions, combined with the serious air pollution problems in many urban areas, Congress made significant changes to the motor vehicle provisions of the CAA and established tighter pollution standards for emissions from automobiles and trucks. These standards were set so as to reduce tailpipe emissions of hydrocarbons, carbon monoxide, and nitrogen oxides on a phased-in basis, beginning in model year 1994. Automobile manufacturers were also required to reduce vehicle emissions resulting from the evaporation of gasoline during refueling.

Fuel quality was also controlled. Scheduled reductions in gasoline volatility and sulfur content of diesel fuel were required for example. Programs requiring cleaner (so-called reformulated) gasoline were initiated in 1995 for the nine cities with the worst ozone problems. Oxygenated fuels with higher levels (2.7%) of ethanol are required to be produced and sold during the winter months in the areas that exceed the federal standard for carbon monoxide.

5.10.3 Air Toxics

Toxic air pollutants are those pollutants that are hazardous to human health or the environment. These pollutants are typically carcinogens, mutagens, and reproductive toxins.

The toxic air pollution problem is widespread. Information generated in 1987 from the Superfund “Right to Know” rule (SARA Section 313) discussed earlier indicated that more than 2.7 billion pounds of toxic air pollutants were emitted annually in the United States during that year. EPA studies indicated that exposure to such quantities of toxic air pollutants may result in 1000–3000 additional cancer deaths each year.

Section 112 of the CAA includes a list of 189 substances that are identified as HAPs. A list of categories of sources that emit these pollutants was prepared and includes: (1) major sources or sources emitting 10 tons/year of any single HAP or a total of 25 tons/year of all HAPs and (2) minor sources (smaller sources, such as dry cleaners and auto body refinishing). In turn, the EPA promulgated emission standards, referred to as maximum achievable control technology or MACT standards, for each listed source category. These standards were based on the best demonstrated control technology (BDCT) or practices utilized by sources that make up each source category. Within 8 years of promulgation of an MACT standard, the EPA must evaluate the level of risk that remains (residual risk) due to exposure to emissions from a source category and determine if the residual risk is acceptable. If the residual risks are determined to be unacceptable, additional standards are required.

5.10.4 Acid Deposition Control

Acid rain occurs when sulfur dioxide (SO_2) and oxides of nitrogen (NO_x) are transformed in the atmosphere to the corresponding sulfuric or nitric acid and return to the earth in the form of rain, fog, or snow. Approximately 20 million tons of sulfur dioxide is emitted annually in the United States, primarily from the burning of fossil fuels by electric utilities. Acid rain damages lakes, harms forests and buildings, contributes to reduced visibility, and is suspected of damaging health.

It was hoped that the CAA would bring about a permanent 10 million ton reduction in SO_2 emissions from 1980 levels. To achieve this, the EPA allocated emission allowances in two phases, permitting utilities to emit 1 ton of sulfur dioxide. The first phase, which became effective January 1, 1995, required 110 power plants to reduce their emissions to a level equivalent to the product of an emission rate of 2.5 lb of SO_2 /MM Btu times the average of their 1985–1987 fuel use. Emissions data indicate that 1995 SO_2 emissions at these units nationwide were reduced by almost 40% below the required level.

The second phase, which became effective January 1, 2000, required approximately 2000 utilities to reduce their emissions to a level equivalent to the product of an emission rate of 1.2 lb of SO_2 /MM Btu times the average of their 1985–1987 fuel use. In both phases, affected sources were required to install systems that continuously monitor emissions in order to track progress and assure compliance.

The CAA allowed utilities to trade allowances within their systems and/or buy or sell allowances to and from other affected sources. Each source must have had sufficient allowances to cover its annual emissions. If not, the source was subject to a \$2000/ton excess emission fee and a requirement to offset the excess emissions in the following year.

The CAA also included specific requirements for reducing emissions of nitrogen oxides.

5.10.5 Operating Permits

The CAA requires the implementation of an operating permits program modeled after the NPDES permit program of the CWA. The purpose of the operating permits program is to ensure compliance with all applicable requirements of the CAA. Air pollution sources subject to the program must obtain an operating permit; states must develop and implement an operating permit program consistent with the act's requirements; and the EPA must issue permit program regulations, review each state's proposed program, and oversee the state's effort to implement any approved program. The EPA must also develop and implement a federal permit program when a state fails to adopt and implement its own program.

In many ways, this program is the most important procedural reform contained in the 1990 Amendments to the CAA. It enhanced air quality control in a variety of ways and updated the CAA, making it more consistent with other environmental statutes. The CWA, RCRA, and FIFRA all require permits.

5.10.6 Stratospheric Ozone Protection

The CAA requires the phase out of substances that deplete the ozone layer. The law required a complete phase out of CFCs and halons, with stringent interim reductions on a schedule similar to that specified in the Montreal Protocol, including CFCs, halons, and carbon tetrachloride by 2000 and methyl chloroform by 2002. Class II chemicals (HCFCs) will be phased out by 2030.

The law required nonessential products releasing Class I chemicals to be banned. This ban went into effect for aerosols and noninsulating foams using Class II chemicals in 1994. Exemptions were included for flammability and safety reasons.

5.10.7 Provisions Relating to Enforcement

The CAA contains provisions for a broad array of authorities to make the law readily enforceable. The EPA has authority to

1. Issue administrative penalty orders up to \$200,000 and field citations up to \$5,000
2. Obtain civil judicial penalties
3. Secure criminal penalties for knowing violations and for knowing and negligent endangerment
4. Require sources to certify compliance
5. Issue administrative subpoenas for compliance data
6. Issue compliance orders with compliance schedules of up to 1 year

Citizen suit provisions are also included to allow citizens to seek penalties against violators, with penalties going to a U.S. Treasury fund for use by the EPA for compliance and enforcement activities.

The following EPA actions represent recent regulations promulgated to implement the requirements of the CAA to achieve significant improvements in air quality, health, and quality of life [10]:

1. *Clean Air Interstate Rule* (70 FR 25161, May 12, 2005). The Clean Air Interstate Rule (CAIR) provided states with a solution to the problem of power plant pollution that drifts from one state to another. The rule uses a cap and trade system to reduce the target pollutants by 70%.
2. *Mercury Rule* (70 FR 28605, May 18, 2005). The EPA issued the Clean Air Mercury Rule (CAMR) on March 15, 2005. This rule builds on the CAIR to reduce mercury emissions from coal-fired power plants, the largest remaining domestic source of human-caused mercury emissions. Issuance of the CAMR marked the first time EPA regulated mercury emissions from utilities and made the United States the first nation in the world to control emissions from this major source of mercury pollution.
3. *Nonroad Diesel Rule* (69 FR 38957, May 11, 2004). The Clean Air Nonroad Diesel Rule (NDR) will change the way diesel engines function to remove emissions and the way diesel fuel is refined to remove sulfur. The rule is one of the EPA's *Clean Diesel Programs*, which were promulgated to produce significant improvements in air quality.
4. *Ozone Rules* (see also <http://www.epa.gov/ozonedesignations/>). The Clean Air Ozone Rules (dealing with 8 h ground-level ozone designation and implementation) designated those areas whose air did not meet the health-based standards for ground-level ozone. The ozone rules classified the seriousness of the problem and required states to submit plans for reducing the levels of ozone in areas where the ozone standards were not being met.
5. *Fine Particle Rules* (see also <http://www.epa.gov/pmdesignations/>). The Clean Air Fine Particles Rules designated those areas whose air did not meet the health-based standards for fine-particulate pollution. This rule required states to submit plans for reducing the levels of particulate pollution in areas where the fine-particle standards were not being met.

More information regarding new initiatives brought about by the CAA Amendments can be found in *15th Anniversary of Clean Air Act Amendments of 1990* at <http://www.epa.gov/air/cleanairact/>

5.10.8 Provisions Relating to Chemical Accidents and Hazards

Regarding hazards of an accident nature, the CAA Amendments of 1990 established two distinct mandates regarding the prevention of chemical accidents in the United States. Section 304 of the CAA Amendments required the OSHA to promulgate a chemical process safety standard to protect employees from hazards associated with accidental releases of highly hazardous substances in the work place. The OSHA promulgated its standard for process safety management (PSM) on February 24, 1992.

Section 112(r) of the CAA Amendments also established requirements related to chemical accident prevention. The purpose of this section is to prevent accidental releases of hazardous substances to the air and to minimize the consequences of releases of those substances. Section 112(r) requires that the EPA promulgate reasonable regulations and appropriate guidance to provide for the prevention and detection of accidental releases and for responses to such releases. Details on Section 112(r) are provided in Section 5.12.

Prior to the adoption of the CAA Amendments, the states of New Jersey, California, and Delaware adopted legislation with requirements for chemical accident prevention at facilities that handle hazardous substances. In 1991, the State of Nevada adopted the Nevada Chemical Catastrophe Prevention Act (NCCPA) in response to two significant chemical accidents within that state. Each of these states has adopted specific requirements regarding accident prevention that have similarities and differences with each other and with the federal laws referred to earlier.

Illustrative Example 5.13

Many acronyms are associated with the CAA and the corresponding amendments. Indicate what each of the following six acronyms stands for

1. NAAQS
2. NSR
3. RFP
4. SIP
5. BACT
6. VOCs

Solution

1. NAAQS=National Ambient Air Quality Standards
2. NSR=New Source Review
3. RFP=Reasonable Further Progress
4. SIP=State Implementation Plan
5. BACT=Best Available Control Technology
6. VOCs=Volatile Organic Compounds

These are but a few of the many acronyms employed in the air pollution regulatory field.

5.11 Occupational Safety and Health Act

The *Occupational Safety and Health Act* (OSHAct) was enacted by Congress in 1970 and established the OSHA, which addressed safety in the workplace. The EPA was established at the same time. Both the EPA and the OSHA are mandated to reduce the exposure of hazardous substances over land, sea, and air. The OSHAct is limited to conditions that exist in the workplace, where its jurisdiction covers both safety and health. Frequently, both agencies regulate the same substances but in a different manner as they are overlapping environmental organizations.

Congress intended that the OSHA be enforced through specific standards in an effort to achieve a safe and healthy working environment. A “general duty clause” was added to attempt to cover those obvious situations that were admitted by all concerned but for which no specific standard existed. The OSHA standards are an extensive compilation of regulations, some that apply to all workers (such as eye and face protection) and some that apply to workers who are engaged in a specific type of work (such as welding or crane operation). Employers are obligated to familiarize themselves with the standards and comply with them at all times.

Health issues, most importantly, contaminants in the workplace, have become OSHA's primary concern. Health problems are complex and difficult to define. Because of this, the OSHA has been slow to implement health standards. To be complete, each standard requires medical surveillance, record keeping, monitoring, and physical reviews. Alternatively, safety hazards are aspects of the work environment that are expected to cause death or serious physical harm immediately or before the imminence of such danger can be eliminated.

Probably one of the most important safety and health standards ever adopted is the OSHA hazard communication standard, more properly known as the “right-to-know” laws. The hazard communication standard requires employers to communicate information to their employees on hazardous chemicals that exist within the workplace. The program requires employers to craft a written hazard communication program, keep *MSDSs* for all hazardous chemicals at the workplace, provide employees with training on those hazardous chemicals, and assure that proper warning labels are in place. This receives additional treatment in Illustrative Examples 6.14 and 8.13.

The *Hazardous Waste Operations and Emergency Response Regulation*, enacted in 1989 by the OSHA, addressed the safety and health of employees involved in cleanup operations at uncontrolled hazardous waste sites being cleaned up under government mandate and in certain hazardous waste treatment, storage, and disposal operations conducted under the RCRA. The standard provides for employee protection during initial site characterization and

analysis, monitoring activities, training, and emergency response. Four major areas fall under the scope of the regulation:

1. Cleanup operations at uncontrolled hazardous waste sites that have been identified for cleanup by a government health or environmental agency
2. Routine operations at hazardous waste Treatment, Storage, and Disposal (TSD) facilities or those portions of any facility regulated by 40 CFR Parts 264 and 265
3. Emergency response operations at sites where hazardous substances have been or may be released
4. Corrective action at RCRA sites

The regulation addressed three specific populations of workers at the aforementioned operations. First, it regulates safety and health standards for workers involved in hazardous substance response operations under the CERCLA, including initial investigations at CERCLA sites before the presence or absence of a hazardous substance has been ascertained; corrective actions taken in cleanup operations under the RCRA; and those hazardous waste operations at sites that have been designated for cleanup by state or local government authorities. The second worker population to be covered involves those employees engaged in operations involving hazardous waste TSD facilities. The third employee population to be covered involves those employees engaged in emergency response operations for release or substantial threat of releases of hazardous substances and postemergency response operations to such facilities, i.e., those regulated under 29 CFR, 1910.120(q) [11].

Congress earlier passed two pieces of legislation for safeguarding worker's health:

1. The Metal and Nonmetallic Mines Safety Act of 1966
2. The Federal Coal Mine Safety and Health Act of 1969

It should also be noted that the OSHA has standards for both ionizing radiation (29 CFR 1910.96) and nonionizing radiation (29 CFR 1910.97).

Illustrative Example 5.14

Differentiate between the EPA and the OSHA.

Solution

EPA and OSHA are both government agencies that have the authority to issue regulations to reduce the exposure of hazardous substances

over land, sea, and air. The OSHA is limited to conditions that exist in the workplace. The OSHA is authorized by the OSHAct to issue regulations that protect workers from the hazardous chemicals they use in manufacturing processes. If these hazardous chemicals are emitted by the plant and affect the surrounding community but do not expose the workers in the plant, the OSHA is not authorized to issue an order to stop the practice. However, this issue would remain within the jurisdiction of the EPA, which is not limited to conditions that exist in the workplace. Frequently, both agencies regulate the same substance but in a different manner. As noted earlier, they are overlapping environmental organizations.

Illustrative Example 5.15

Describe the difference between the *OSHAct* and the *OSHA*.

Solution

The OSHAct was enacted by Congress in 1970 and established the OSHA, which addressed safety in the workplace. Both the EPA and the OSHA are mandated to reduce the exposure of hazardous substances over land, sea, and air. The OSHAct is limited to conditions that exist in the workplace, where its jurisdiction covers both safety and health. As noted earlier, both agencies often regulate the same substance but in a different manner as they are overlapping environmental organizations. Congress intended that the OSHAct be enforced through specific standards in an effort to achieve a safe and healthy working environment.

5.12 EPA's Risk Management Program

Developed under the aforementioned CAA's Section 112(r), the *Risk Management Program* (RMP) rule (40 CFR Part 68) is designed to reduce the risk of accidental releases of acutely toxic, flammable, and explosive substances. A list of the regulated substances (138 chemicals) along with their threshold quantities is provided in the CFR at 40 CFR 68.130.

In the RMP rule, the EPA requires a *Risk Management Plan* (RMP) that summarizes how a facility is to comply with EPA's RMP requirements. It details methods and results of the hazard assessment, accident prevention, and emergency response programs instituted at the facility. The hazard assessment step shows the area surrounding the facility and the population potentially affected by accidental releases. EPA requirements include a three-tiered approach for affected facilities. A facility is affected if a process unit manufactures, processes, uses, stores, or otherwise handles any of the

TABLE 5.2

RMP Tier Approach

Tier	Description
1	Facilities submit RMP, complete registration of processes, analyze worst-case release scenario, complete 5 year accident history, coordinate with local emergency planning and response agencies, and certify that the source's worst-case release would not reach the nearest public receptors
2	Facilities submit RMP, complete registration of processes, develop and implement a management system, conduct a hazard assessment, implement certain prevention steps, develop and implement an emergency response program, and submit data on prevention program elements
3	Facilities submit RMP, complete registration of processes, develop and implement a management system, conduct a hazard assessment, implement prevention requirements, develop and implement an emergency response program, and provide data on prevention program elements

listed chemicals at or above the threshold quantities. The EPA approach is summarized in Table 5.2.

For example, the EPA defined Tier 1 facilities as those that have not had an accidental release with offsite consequences in the 5 years prior to the submission date of the RMP and have no public receptors within the distance to a specified toxic or flammable endpoint associated with a worst-case release scenario. Tier 1 facilities have to develop and submit a RMP and complete a registration that includes all processes that have a regulated substance present in more than a threshold quantity. They also have to analyze the worst-case release scenario for the process or processes; document that the nearest public receptor is beyond the distance to a toxic or flammable endpoint; complete a 5 year accident history for the process or processes; ensure that response actions are coordinated with local emergency planning and response agencies; and certify that the source's worst-case release would not reach the nearest public receptors.

Tier 2 applies to facilities that are not Tier 1 or Tier 3 facilities. Tier 2 facilities have to develop and submit the RMP as required for Tier 1 facilities plus develop and implement a management system; conduct a hazard assessment; implement certain prevention steps; develop and implement an emergency response program; and submit data on prevention program elements for Tier 2 processes.

Tier 3 applies to processes in SIC codes 2611 (pulp mills), 2812 (chloralkali), 2819 (industrial inorganics), 2821 (plastics and resins), 2865 (cyclic crudes), 2869 (industrial organics), 2873 (nitrogen fertilizers), 2879 (agricultural chemicals), and 2911 (petroleum refineries). These facilities belong to industrial categories identified by the EPA historically accounting for most industrial accidents resulting in off-site risk. Tier 3 also applies to all processes subject to the OSHA PSM standard (29 CFR 1910.119). Tier 3 facilities have to develop and submit the RMP as required for Tier 1 facilities plus develop and implement

a management system; conduct a hazard assessment; implement prevention requirements; develop and implement an emergency response program; and provide data on prevention program elements for Tier 3 processes.

EPA's goals in developing this rule included requiring industry to both understand and take responsibility for potential hazards present in their facilities, to upgrade existing systems and address new facilities with prevention and mitigation of potential hazards in mind, and to open dialogue between industry and the community they were adjacent to. EPA's focus was on major chemical accidents and how they can affect the environment both on- and offsite.

Illustrative Example 5.16

Define worst-case scenario as it relates to RMP regulations.

Solution

The definition of worst-case scenario is arguably the most controversial aspect of the RMP regulations and is still the subject of much debate. In the initial proposed rule (October 20, 1993), facilities were to determine the worst-case scenario by the following:

*... assume that all the regulated substance in the process
is instantaneously released and all mitigation systems
fail to minimize the consequences of the release.*

This definition was argued to be unrealistic as it is normally not feasible to lose all the material in a process instantaneously and would not provide any useful information to the public. In the supplemental rule (March 13, 1995), the definition was changed to

*... the release of the largest quantity of a regulated substance
resulting from a vessel or process piping failure.*

Additionally, the analysis for worst case would entail a 10 min release under worst-case weather conditions, that is, F stability (see Chapter 10) and 1.5 m/s wind speed. The rule is considering the inclusion of the effects of passive mitigation measures for the worst-case scenario. Passive mitigation systems include dikes, catch basins, and drains for liquid, as well as enclosures for liquids and gases. Active mitigation system effects are not to be included when analyzing the worst-case scenario but are being considered for the other more likely scenarios.

Illustrative Example 5.17

Describe the overall objective of the RMP rule.

Solution

The RMP rule is designed to reduce the risk to adjacent communities of accidental releases of acutely toxic, flammable, and explosive substances from regulated industries.

Illustrative Example 5.18

List the four principal agencies that regulate risk issues in the United States.

Solution

The four main agencies regulating human health and environmental risk in the United States include

1. The EPA, an independent agency, which administers air, water, and toxic substance legislation.
2. The OSHA, a part of the Department of Labor, which sets exposure standards and safety rules for work places.
3. The Food and Drug Administration (FDA), which regulates foods, drugs, and cosmetics. It is housed in the Department of Health and Human Services and reports to the Assistant Secretary for Health.
4. The CPSC, an independent agency, which controls the packaging, labeling, and distribution of a broad range of toys, clothes, electronics, and other products.

Illustrative Example 5.19

List several elements of an RMP as required by the CAA.

Solution

Ten of the more important required elements of an RMP as required by the CAA include

1. Hazard review
2. Process safety information
3. Standard operating procedures
4. Training
5. Maintenance
6. Accident investigation
7. Process hazard analysis
8. Pre-startup review
9. Management of change
10. Audits

Details on these elements of an RMP are presented in Ref. [12].

Illustrative Example 5.20

Provide a table of contents for the Accidental Release Prevention Requirements; Risk Management Programs Under the CAA Section 112(r)(7); and Distribution of Off-Site Consequence Analysis (OCA) Information.

Solution

This rule was published in the Federal Register on August 4, 2000, following a proposed rule on April 27, 2000. The table of contents for the rule is found to be as follows:

Table of Contents

- I. Introduction
 - A. Statutory Authority and Background
 - B. The Proposed Rule
- II. Discussion of Comments on the Proposed Rule
 - A. Risk and Benefits Assessment
 - 1. Benefits Assessment
 - 2. Risk Assessment
 - 3. The Assessments and the Proposed Rule
 - B. General Comments on the Rule
 - C. Rule's Impact on Risk Reduction
 - D. Reading Rooms
 - 1. General Comments on Reading Rooms
 - 2. The Number of Paper Copies
 - 3. Operations of Reading Rooms
 - 4. The Number of Reading Rooms
 - 5. The Location of Reading Rooms
 - 6. Security Measures at Reading Rooms
 - 7. Alternatives to Reading Rooms
 - E. Enhanced Local Access to OCA Information
 - F. Risk Indicators System (Vulnerable Zone Indication System)
 - G. Internet-Accessible OCA Information
 - H. Access to OCA Information by Government Officials
 - I. Other Provisions
- III. Discussion of Final Rule
 - A. Access to Paper Copies of OCA Information
 - B. Enhanced Access to Local OCA Information
 - C. Vulnerable Zone Indicator System
 - D. Internet Access to Selected OCA Information
 - E. Additional Information on Chemical Accident Risk
 - F. Access to OCA Information by Government Officials and Other Provisions
 - G. Effective Date and Implementation Schedule
- IV. Administrative Requirements
 - A. Docket
 - B. Executive Order 12866
 - C. Executive Order 12988
 - D. Executive Order 13045
 - E. Executive Order 13084
 - F. Executive Order 13132
 - G. Regulatory Flexibility Act
 - H. Paperwork Reduction Act

- I. Unfunded Mandates Reform Act of 1995
- J. Small Business Regulatory Enforcement Fairness Act of 1996
- K. Congressional Review Act
- L. Judicial Review

A comprehensive treatment of all of the aforementioned laws and regulations, the most important of which is the RMP, is available in Ref. [13]. As one might suppose, the RMP regulations represent a significant regulatory program. Some websites that provide additional information on these RMP regulations include

1. www.epa.gov/emergencies
2. www.epa.gov/emergencies/content/rmp/index.htm
3. www.epa.gov/ttn/
4. www.osha.gov/SLTC/processsafetymanagement/index.html
5. www.nfpa.org

In addition, the New Jersey Toxic Catastrophic Prevention Act (TCPA) receives treatment in Section 6.9.1.

5.13 Pollution Prevention Act of 1990

The Pollution Prevention (P2) Act, along with the CAA Amendments passed by Congress on the same day in November 1990, represents a clear breakthrough in this nation's understanding of environmental problems. The P2 Act calls pollution prevention a "national objective" and establishes a hierarchy of environmental protection priorities as national policy.

Under the P2 Act, it is the national policy of the United States that pollution should be prevented or reduced at the source whenever feasible; where pollution cannot be prevented, it should be recycled in an environmentally safe manner. In the absence of feasible prevention and recycling opportunities, pollution should be treated, and disposal should be used only as a last resort.

Among other provisions, the P2 Act directed the EPA to facilitate the adoption of source reduction techniques by businesses and federal agencies to establish standard methods of measurement for source reduction, to review regulations to determine their effect on source reduction, and to investigate opportunities to use federal procurement to encourage source reduction. The act initially authorized an \$8 million state grant program to promote source reduction, with a 50% state match requirement to receive federal funds [14].

The EPA's pollution prevention initiatives are characterized by its use of a wide range of tools, including market incentives, public education and information, small business grants, technical assistance, research and technology applications, as well as more traditional regulations and enforcement. In addition, there are other significant behind-the-scenes achievements involving identifying and dismantling barriers to pollution prevention, laying the groundwork for a systematic pollution prevention focus, and creating advocates for pollution prevention that serve as catalysts in a wide variety of institutions.

Illustrative Example 5.21

List the advantages of applying the pollution prevention principles set down by the P2 Act of 1990 to an environmental management program.

Solution

The advantages of applying pollution prevention principles to an environmental management program are as follows [15,16]:

1. The P2 Act of 1990 calls on companies to disclose and report a great deal about their operations, as opposed to requiring widespread inspections to determine compliance that would be very expensive. Mandating required inspections also would severely strain federal, state, and local government's manpower.
2. The law aims at creating a more cooperative relationship between the environmental agencies and industry. Strict enforcement provisions with penalties for incomplete compliance could do the opposite and actually create a disincentive to critical self-auditing, self-policing, and voluntary disclosure.
3. Companies have an incentive to voluntarily comply with the law because having smaller quantities of chemicals to dispose of could actually save money while giving the company a public relations edge over its competition.

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6

Emergency Planning and Response

6.1 Introduction

This chapter addresses planning for emergencies and how to respond appropriately when they occur. Although much of the material in this chapter may appear to be dated, the response procedures in place still apply. The reader should note that the presentation is geared primarily for local and state personnel. However, the same basic approach is applied to planning and response activities for industrial applications.

The next section explains some reasons for planning ahead and discusses laws that require community groups to develop emergency response plans. Regardless of the existence of such laws, however, it makes good sense to plan ahead. Once an explosion has occurred, for example, it is probably too late for analysis. The topic of the following section is the planning committee; this group should be composed of people who can make it successful, i.e., government leaders, industry specialists, police, firefighters, health specialists, and local residents. Section 6.4 describes the hazards survey. Before a plan can be developed, an inventory of the potential hazards in a community must be gathered; then the risks associated with each hazard must/can be assessed and prioritized.

The main section of this chapter can be found in Section 6.5. It details the items that should be included in an emergency plan, which specifies the actions to be taken during an emergency and identifies the critical personnel and their responsibilities. A clear, concise, stepwise approach is the goal of the emergency plan. The next section discusses training. Service groups need to be trained for emergencies before such events occur. Public officials should be apprised of their roles in emergencies. Communications during an emergency (Section 6.7) is critical. Notification of the proper government agencies is required by law; a clearly understood and well-publicized notice is important to control the public's response. The manner in which information regarding an emergency is communicated can be just as crucial as the information itself. Many injuries and deaths during a disaster are the result of panic, which is often triggered by misinformation or a lack of information.

The implementation of the plan (Section 6.8) includes the need to keep it current. An occasional audit is imperative to keep the plan from becoming obsolete [1]. This chapter concludes with a short section that examines state initiatives on both environmental management and emergency response planning. It should also be noted that all of the illustrative examples appear at the end of the chapter because of the overlapping nature of many of the aforementioned topics.

Some of this material appeared in Chapter 5, and the reader may choose to review that chapter before proceeding with the material that follows.

6.2 Need for Emergency Response Planning

Emergencies have occurred in the past and will continue to occur in the future. A few of the many common sense reasons to plan ahead are provided in the following [2]:

1. Emergencies will happen; it is only a question of time.
2. When emergencies occur, the minimization of loss and the protection of people, property, and the environment can be achieved through the proper implementation of an appropriate emergency response plan.
3. Minimizing the losses caused by an emergency requires planned procedures, understood responsibility, designated authority, accepted accountability, and trained and experienced people. With a fully implemented plan, these goals can be achieved.
4. If an emergency occurs, it may be too late to plan. Lack of preplanning can turn an emergency into a disaster.

A particularly timely reason to plan ahead is to ease the “chemophobia,” or fear of chemicals, which is so prevalent in society today. So much of the recent attention to emergency planning and so many newly promulgated laws are a reaction to the tragedy at Bhopal. The probable causes of “chemophobia” are lack of information and misinformation. Fire is hazardous, and yet it is used regularly at home. Most adults have understood the hazards associated with fire since the time of the caveman. By the same token, hazardous chemicals, necessary and useful in modern society, are not something to fear. Chemicals need to be carefully used and their hazards understood by the general public. A well-designed emergency plan that is understood by the individuals responsible for action, as well as by the public, can ease concerns over emergencies and reduce “chemophobia.” People will react during an emergency; how they react can be somewhat controlled through

education. When ignorance is pervasive, the likely behavior during an emergency is panic.

An emergency plan can minimize loss by helping to assure the proper responses. "Accidents become crises when subsequent events, and the actions of people and organizations with a stake in the outcome, combine in unpredictable ways to threaten the social structures involved" [3]. The wrong response can turn an accident into a disaster as easily as no response. For example, if a chemical fire is doused with water, which causes the emission of toxic fumes, it would have been better to let the fire burn itself out. For another example, suppose people are evacuated from a building into the path of a toxic vapor cloud; they might well have been safer staying indoors with closed windows. Still another example is offered by members of a rescue team who become victims because they were not wearing proper breathing protection. The proper response to an emergency requires an understanding of the hazards. A plan can provide the right people with the information they need to respond properly during an emergency.

In addition to the aforementioned commonsense reasons, there are legal reasons to plan. Recognizing the need for better preparation to deal with chemical emergencies, Congress enacted the Superfund Amendments and Reauthorization Act of 1986 (SARA), discussed in detail in Chapter 5. One part of the SARA is the aforementioned stand alone act called *Title III* (the Emergency Planning and Community Right-to-Know Act [EPCRA] of 1986). This act requires federal, state, and local governments and industry to work together in developing emergency plans and "community right-to-know" reporting on hazardous chemicals. These new requirements build on EPA's Chemical Emergency Preparedness Program and numerous state and local programs that are aimed at helping communities deal with potential chemical emergencies [1].

Most large industries have long had emergency plans designed for on-site personnel. The protection of people, property, and, thus, profits has made emergency plans and prevention methods common in industry. On-site emergency plans are also often required by insurance companies. One way to minimize the effort required for emergency planning is to expand existing industry plans to include all significant hazards and all people in a given community.

6.3 Planning Committee

Emergency planning should grow out of a team process coordinated by a leader. The team may be the best vehicle for including in the planning process people representing various areas of expertise, thus producing a more meaningful and complete plan. The team approach also encourages planning that will reflect a consensus of the entire community. Some individual

communities and areas that included several communities had formed advisory councils before SARA requirements. These councils can serve as an excellent resource for the planning team recommended for SARA planning activities [4].

The following considerations are important when selecting the members of a team that will bear overall responsibility for emergency planning:

1. Emergencies will happen; it is only a question of time.
2. The group must possess, or have ready access to, a wide range of expertise relating to the community, its industrial facilities, its transportation systems, and the mechanics of emergency response and response planning.
3. The members of the group must agree on their purpose and be able to work cooperatively.
4. The group must be representative of all the elements of the community that have substantial interest in reducing the risks posed by emergencies.

While many individuals have an interest in reducing the risks posed by hazards, their differing economic, political, and social perspectives may cause them to favor different means of promoting safety. For example, people who live near an industrial facility that manufactures, uses, or emits hazardous materials are likely to be greatly concerned about avoiding threats to their lives. They are likely to be less concerned about the costs of developing accident prevention and response measures than some of the other team members. Others in the community, for example, those representing industry or the budgeting group are likely to be more sensitive to costs. They may be more anxious to avoid expenditures for unnecessarily elaborate prevention and response measures. Also, industry facility managers, although concerned with reducing risks posed by hazards, may be reluctant, for proprietary reasons, to disclose materials and process information beyond what is required by law. These differences can be balanced by a well-coordinated team that is responsive to the needs of its community.

Agencies and organizations bearing emergency response responsibilities may have differing views about the role they should play in case of an incident. The local fire department, an emergency management agency, and a public health agency are all likely to have some responsibilities during an emergency. However, each of these organizations might envision a very different set of actions at the emergency site. The plan will serve to detail the actions of each response group during an emergency.

In organizing the community to address the problems associated with emergency planning, it is important to bear in mind that all affected parties have a legitimate interest in the choices among planning alternatives. Therefore, strong efforts should be made to ensure that all such groups are included in

the planning process. The need for unity of the committee during both the planning and the implementation processes increases for larger numbers of different community groups. Each group has a right to participate in the planning, and a well-structured, well-organized planning committee should serve the entire community.

By law, the planning committee should include the following [5]:

1. Elected and state officials
2. Civil defense personnel
3. First aid personnel
4. Local environmental personnel
5. Transportation personnel
6. Owners and operators of facilities subject to the SARA
7. Law enforcement personnel
8. Firefighting personnel
9. Public personnel
10. Hospital personnel
11. Broadcast and print media
12. Community groups

Other individuals who could also serve the community well and should be a part of the committee include technical professionals, city planners, academic and university researchers, and local volunteer help organizations [6].

The local government has a great share of the responsibility for emergency response within its community. The official who has the power to order evacuation, fund fire and emergency units, and educate the public is a key person to emergency planning and the resulting response effort. For example, an entire plan might fail if a necessary evacuation were not ordered on time. Although politics should be disassociated from technical decisions, such linkage is inevitable in emergency planning. Distasteful options that require political courage are often necessary. In a given situation, for example, one may need to decide whether to evacuate a section of town where there is some doubt about the necessity of evacuation, but the worst-case consequence of not evacuating would be deadly. A public official can build support for future candidacy by using the issue of chemical safety as a bandwagon, but mistakes in handling emergencies are measured by a strong instrument, e.g., the election, and a failed emergency plan can be fatal to a political career. Politics is a social feedback device which, when used properly, can aid government leaders in making correct decisions. A political career can also be destroyed by an error in reading the social feedback. An effective plan can save elected officials' hours of media criticism after a crisis because the details of a response were organized by someone on

the team before events occurred. Because of the power elected officials have locally, they are likely to take the leadership roles on such committees.

The independence of fire and police units from political control is somewhat traditional. Recognition of the freedom necessary to conduct public safety work gives police and fire units the option of rejecting outside control. However, to be successful, community emergency response planning must be universally developed and implemented. The fire and police departments, which are likely to be first on the emergency scene, will be required to act immediately. Their knowledge of the hazards and the plan is important to the plan's effectiveness as well as to their own safety. The police are best suited for evacuation and crowd control or protection of evacuated areas. They will need to understand all such assigned roles. The fire service groups will likely be on the scene to control the effects of the accident. The fire service people must bring to the committee their expertise for treating emergencies, a real asset. The firefighters must also learn from the committee the special considerations to be given to emergencies other than structural fires.

The environmental agencies may be among the best suited for evaluating risk. Their expertise usually includes a sound knowledge of the particular features of the local environment, such as location of flood plains and water resources, and the hazards of certain chemicals. They should be used to support the risk evaluation effort. The local or state environmental agencies are also a source for inventory of hazards on industrial sites. This information will serve the committee.

The state or local health agencies will help the committee to understand adverse health effects. For example, the risks associated with different chemicals can be evaluated by health agency personnel or by their contacts at universities and research institutions. These experts can assist in evaluating the health risks of various hazards. The owners and operators of facilities handling hazardous chemicals can be an asset in emergency planning because of their knowledge of the safety features already in place. The representatives of industry also have access to information about the hazards of each chemical, either from the supplier or from the company's research department. Knowledge of on-site prevention features at an industrial site can help to sort through the potential hazards listed and to focus on the significant ones.

The local planners in a city or community may also be equipped to assist in emergency planning. The agendas of these groups typically include developing the community, creating jobs, and establishing economic stability; thus, the planners have their own reasons for wanting a community to be viewed as safe. The planners are also likely to have detailed information about the community, that not only includes road maps and transportation routes but also locations of highly populated areas and industrial sections. The understanding of the locations of people and places in a community is important to planning and assessing the significant risks posed to the community.

The local planners can serve the committee because of their knowledge of these demographic and industry-related features of their community.

Toxicologists, meteorologists, chemists, plus environmental and chemical engineers are among the technical professionals who have experience and knowledge about chemicals, hazards, and preventive designs. The committee needs individuals with such expertise to assist in the preparation of plans that are technically and scientifically sound as well as safe. The evaluation of hazards and the design of appropriate emergency responses should reflect rational choices, not political options.

The management or control of the committee during planning, and especially during implementation, is essential. As suggested earlier, it is a given that the emergency plan will be generated by different individuals with different priorities. The different groups will have their own legitimate interests, and each interest will have to be weighed against its value to the plan. The committee leader must demonstrate respect for the interests of each of the individuals, as well as for each member's contributions. The committee leader is likely to be chosen for several reasons, including the following:

1. The degree of respect held for the person by groups and individuals with an interest in the emergency plan
2. The time and resources the person will be able to devote to the work of the committee
3. The person's history of working relationships with concerned community agencies and organizations
4. The person's management and communication skills
5. The person's present responsibilities and background related to emergency planning, prevention, and response

Personal considerations, as well as institutional ones, should be weighed when selecting a committee leader. If one candidate has all the right resources to address the issues of emergency planning and implementation but is unable to interact with local officials, someone else may be a better choice. Since the committee leader must coordinate this large group of people with different priorities and realms of expertise, the choice of the leader is critical to the success of the committee [7].

6.4 Hazards Survey

A survey of hazards or foreseeable threats in the community must be performed and evaluated to characterize potential disasters by type and extent. Without such information, an appropriate plan cannot be developed.

An inventory of the community protection assets, hazard sources, and risks must be completed before the actual plan is written. The procedures followed here are similar to those provided in Chapter 13.

Although a plan for a city divided by a river may not be applicable to a desert city on a seismic fault, duplication can be an enemy of cost efficiency. Thus, wherever possible, any emergency plans that already exist in the community should be used as a starting point. Community groups that may have developed such plans include civil defense organizations, fire departments, the Red Cross, public health agencies, and local industry councils. Existing plans should be studied and their applicability to the proposed community plan evaluated.

Local government departments, such as those dealing with transportation, water, power, and sewer, may have valuable resources. These should be listed and then compared to the needs of the plan. Some resource examples are provided in the following:

1. Trucks
2. Equipment (e.g., backhoes and flatbeds)
3. Laboratory services (e.g., water department)
4. Fire vehicles
5. Police vehicles
6. Emergency suits
7. Breathing apparatus
8. Gas masks
9. Number of trained emergency people
10. Number of volunteer personnel (e.g., Red Cross)
11. Buses or cars
12. Communication equipment (e.g., hand radios)
13. Local TV and radio stations
14. Ambulances
15. Trained medical technicians and first aid personnel
16. Stocks of medicines
17. Burn treatment equipment
18. Fallout shelters

The potential sources of hazards should be listed for risk assessment. The SARA requires certain industries to provide information to the planning committee. Information about small as well as large industries is necessary to permit the committee to evaluate *all* of the significant hazard risks to the community. The information required by the SARA (some of which was provided in Chapter 5) includes

1. The chemical name
2. The quantity stored over a period of time
3. The type of chemical hazard (e.g., toxicity, flammability, ignitability, and corrosivity)
4. Chemical properties and characteristics (e.g., liquid at certain temperatures, gas at certain pressures, and reacts violently with water)
5. Storage description and storage location on the site
6. Safeguards or prevention measures associated with the hazardous chemical storage or handling design, such as dikes, isolation of incompatible substances, fire resistant equipment, etc.
7. Control features for prevention such as temperature and pressure controllers and fail-safe design devices, if included in the handling design
8. Recycle control loops intended for accident prevention
9. Emergency shutdown features

The planning committee should designate hazard sources on a community map. This information probably already exists and can be obtained locally from the transportation department, environmental protection agency, city planning department, community groups, and industry sources. Some of the data to be represented on the community map are

1. Industrial and other sites of possible chemical accidents
2. Wastewater and water treatment plants in which chlorine is stored
3. Potable and surface water
4. Drainage and runoff
5. Population location and density in different areas
6. Transportation routes for children
7. Commuter routes
8. Truck transport roads
9. Railroad lines, yards, and crossings
10. Major highways, noting merges, and downhill curves
11. Hospitals and nursing homes
12. Fallout shelters

The potential for natural disasters, based on the history and knowledge of the region and local geology, should also be indicated in the plan. Items such as seismic fault zones and flood plains and potentials for hurricanes, tornadoes, and winter storms should be noted.

The risk inventory or risk evaluation is the next part of the hazard survey. It is not practical to expect the plan to cover every potential accident. When the hazards have been evaluated, the plan should be focused on the most significant ones. This risk assessment stage requires the technical expertise of many people in order to compare the pieces of data and determine the relevance of each. Among the important factors to be considered in performing the risk evaluation are the following:

1. The routes of transport of hazardous substances should be reviewed to determine where a release could occur.
2. Industry sites are not the only sources of hazards; thus, the proximity of hazards to people and other sensitive environmental receptors should be examined.
3. The toxicology of different exposure levels should be reviewed.

When the significant risks have been listed, the hazard survey is complete and the plan can be developed.

6.5 Plan for Emergencies

Successful emergency planning begins with a thorough understanding of the event or potential disaster being planned for. The impacts on public health and the environment must also be estimated. Some of the emergencies that should be included in the plan are [8]:

1. Earthquakes
2. Explosions
3. Fires
4. Floods
5. Hazardous chemical leaks, both gas or liquid
6. Power or utility failures
7. Radiation incidents
8. Tornadoes or hurricanes
9. Transportation accidents

Some of these “emergencies” are addressed in Chapter 13 and in several of the case studies in Part IV.

The likely emergency zone must be studied to estimate the potential impact on the public or the environment of accidents of different types. For

example, a hazardous gas leak, fire, or explosion may cause a toxic cloud to spread over a great distance. The minimum affected area, and thus the area to be evacuated, should be estimated on the basis of an atmospheric dispersion model. Various models can be used; the more complex models often produce more realistic results, but the simple and faster models may provide adequate data for planning purposes [9]. A more thorough discussion of atmospheric dispersion is presented in Chapter 10.

In formulating the plan, some general assumptions may be made:

1. Organizations do a good job when they have specific assignments.
2. The various resources will need coordination.
3. Most of the necessary resources are likely to be already available in the community (in plants or city departments).
4. People react more rationally when they have been apprised of a situation.
5. Coordination is basically a social process, not a legal one.
6. Disorganization and reorganization are common in a large group.
7. Flexibility and adaptability are basic requirements for a coordinated team.

The objective of the plan should be a procedure that uses the combined resources of the community in a way that will:

1. Safeguard people during emergencies
2. Minimize damage to property and the environment
3. Initially contain the incident and ultimately bring it under control
4. Effect the rescue and treatment of casualties
5. Provide authoritative information to the news media (for transmission to the public)
6. Secure the safe rehabilitation of the affected area
7. Preserve relevant records and equipment for subsequent inquiry into causes and circumstances

During the development of the plan, the assumptions and objectives should be kept in mind. Although prevention is an important goal in accident and emergency management, it is not really the objective of this plan. The plan should focus on minimizing damage when emergencies occur [2]. Key components of the emergency action plan include the following [1]:

1. Emergency actions other than evacuation
2. Escape procedures when necessary

3. Escape routes clearly marked on a site map, and perhaps also on the roads
4. A method of accounting for people after evacuation
5. Description and assignment of rescue and medical duties
6. A system for reporting emergencies to the proper regulatory agencies
7. A means of notification of the public by an alarm system
8. Responsibilities of contact and coordination person

The SARA originally called for each community group, as designated by the governor, to have a plan by 1988. Specific requirements included the following:

1. Identification of all facilities as well as transportation routes for extremely hazardous substances (EHSs)
2. Establishment of emergency response procedures, both on and off plant sites (facility owner and operator actions, as well as the actions of local emergency and medical personnel)
3. Establishment of methods of determining when releases occur and what areas and populations may be affected by them
4. Listing of community and industry emergency equipment and facilities, along with the names of those responsible for the equipment and its upkeep
5. Description and scheduling of a training program to teach methods for responding to chemical emergencies
6. Establishment of methods and schedules for exercises or drills to test emergency response plans
7. Designation of a community coordinator and a facility coordinator to implement the plan
8. Designation of facilities (e.g., hospitals and natural gas plants) that are subject to added risk, and provision for their protection

A standard format that could be followed might incorporate the following:

1. A statement promulgating the plan
2. A purpose for the plan
3. Assumptions made in developing the plan
4. A discussion of the plan's weaknesses and vulnerabilities
5. A clear statement of when the plan will be executed
6. A stepwise narrative explanation of how the plan works (for those who will direct or coordinate the plan)

7. A chart of the major disaster functional groups, including the departments and volunteers who are responsible for coordinating or supporting each function
8. A description of the responsibilities of each functional group (e.g., duties and actions of police)
9. A list of the necessary equipment, its location, and contact persons for obtaining each item or unit
10. A method for communicating each type of emergency to the public, the functional groups, and the responsible agencies
11. A list of the emergency coordinator's tools and/or resources
12. Training details and schedules
13. The plan implementation schedule, including slots for routine audits and updates

Different emergencies are likely to require different response actions. Specific steps for coping with four types of emergency situations are outlined below:

1. Volatile toxic release
 - a. Release should be deluged with water.
 - b. People who will possibly be affected by the toxic cloud should be warned to close their windows or, if necessary, evacuated.
 - c. Police with protective equipment should check the homes that have been affected.
2. Flammable chemical fire
 - a. Access to the area should be controlled.
 - b. Fire should be prevented from spreading.
 - c. Fire should be extinguished by professionals using proper personal protective gear and modern firefighting equipment.
3. Chemical spill
 - a. Spilled substance should be contained.
 - b. Medical personnel with protective equipment should be available to administer to those affected.
 - c. Rescue team with protective equipment should collect the spilled material in containers.
4. Tornado
 - a. Emergency warnings should be issued to people to move to shelters.
 - b. Equipment in factories should be shut down.
 - c. Squads of rescue teams should be rushed to the affected areas after the tornado has passed.

The details of the plan will be different from community to community, and the appropriate responses will differ according to the event anticipated. Obviously, each community must develop a plan tailored to its own needs.

6.6 Training of Personnel

The education of the public is critical to securing public support of the emergency plan; the real hazards in the community must be made known, as well as what to do in an emergency. Most people are not aware of the reality of hazards in their communities. The common perception is that hazards exist elsewhere, as do the resulting emergencies [10]. The education of the populace about the true hazards associated with routine discharges from plants in the neighborhood and preparing that populace for emergencies is a real challenge to the community committee. People must be taught how to react to an emergency, i.e., how to recognize and report an incident, how to react to alarms, and what other action to take. A possible initial result of SARA Title III may be a fear of industrial discharges on the part of the public [11]. News stories can be misleading if based on hazardous chemical inventories, accidental release data, or annual emissions reports of questionable accuracy or if taken out of context. It should be possible to put such information into perspective through training programs.

The personnel at an industrial plant who are trained in the operation of the facility are critical to proper emergency response. They must be taught to recognize abnormalities in operations and to report them immediately. Plant operators should be taught how to respond to various types of accidents. Internal emergency squads can also be trained to contain the emergency until outside help arrives or, if possible, to eliminate the emergency all together. It is especially important to train plant personnel in shutdown and evacuation procedures.

Training is important for the emergency teams to assure that their roles are clearly understood and that accidents can be responded to safely and properly without delay. As discussed earlier, the emergency teams include the police, fire, and medical personnel, and the volunteers who will be required to take action during an emergency [11]. These people must be knowledgeable about the potential hazards. For example, specific antidotes for different health-related conditions must be known by medical personnel prior to any potential accident. The entire emergency team must also be taught the use of personal protective equipment.

Local government officials also need training. Since these officials have the power to order an evacuation, they must be aware of the circumstances under which such action is necessary, and they must understand before an

emergency occurs that the timing of an evacuation is critical. Local officials also control the use of city equipment and therefore must know what is needed for an appropriate response to a given emergency.

Media personnel, such as print and broadcast reporters, editors, etc., must also be involved in the training program since it is important that the public receive accurate information. If incorrect or distorted information about an emergency is disseminated, panic can easily result. For this reason, it is important for print and broadcast journalists to be somewhat knowledgeable about the potential hazards and the details of emergency responses.

Training for emergencies should be done routinely:

1. When a new member is added to the group
2. When someone is assigned a new responsibility within the community
3. When new equipment or materials are acquired for use in emergency response
4. When emergency procedures are revised
5. When a practice drill shows inadequacies in performance of duties
6. At least once annually

Any training program should address five questions.

1. How are potential hazards recognized? (This can be determined by periodic review of hazards and prevention measures.)
2. What precautions (e.g., donning personal protective equipment) are to be taken when responding to an emergency?
3. Where are the evacuation routes?
4. To whom should a hazard be reported?
5. What actions constitute proper responses to special alarms or signals?

It is important for emergency procedures to be performed as planned. This requires regular training to ensure that people understand and remember how to react. The best plan on paper is likely to fail if the persons involved are reading it for the first time as an emergency is occurring. People must be trained *before* an emergency happens.

6.7 Notification of Public and Regulatory Officials

Notifying the public of an emergency is a task that must be accomplished with caution. People will react in different ways when receiving notification

of an emergency. Many will simply not know what to do, some will not take the warning seriously, and others will panic. Proper training in each community, as discussed in the previous section, can help minimize panic and can condition the public to make the correct response in a time of stress.

Methods of communicating an emergency will differ from community to community, depending on its size and resources. Some techniques for notifying the public are:

1. The sounding of fire department alarms in different ways to indicate emergencies of certain kinds
2. Chain phone calls (this method usually works well in small towns)
3. Announcements made through loudspeakers from police cars or the vehicles of volunteer teams

Once the emergency has been communicated, an appropriate response by the public must be evoked. For this to occur, an accepted plan that people know and understand must be put into effect. Since an emergency can quickly become a disaster if panic ensues, the plan should include the appropriate countermeasures to bring the situation back under control.

Information reported to the emergency coordinator must be carefully screened. A suspected "crank call" should be checked out before an alarm is sounded. By taking no immediate action, however, the team runs the obvious risk that the plan will not be implemented in time. Therefore, if a call cannot be verified as bogus, a response must begin and local police should be dispatched quickly to the scene of the reported emergency to provide firsthand information of the actual situation.

The print and broadcast media can be a major resource for communication, and one job of the emergency coordinator is to prepare information for reporters. The emergency plan should include a procedure to pass along information to the media promptly and accurately.

Certain types of emergencies must be reported to government agencies; it is not always sufficient to notify just the response team. For example, state and federal laws require the reporting of hazardous releases and nuclear power plant problems. There are also more specific requirements under SARA Title III for reporting chemical releases. Facilities that produce, store, or use a listed hazardous substance must immediately notify the Local Emergency Planning Committee (LEPC) and the State Emergency Response Commission (SERC) if there is a release of one or more substances specifically listed in the SARA. These substances include 402 extremely hazardous chemicals on the list prepared by the *Chemical Emergency Preparedness Program* and chemicals subject to the reportable quantities requirements of the original Superfund [1]. The initial notification can be made by telephone, radio, or in person. Emergency notification requirements involving transportation incidents can be satisfied by dialing 911 or calling the

operator. The emergency planning committee should provide a means of reporting information on transportation accidents quickly to the emergency coordinator.

The SARA requires that the notification of an industrial emergency include

1. The name of the chemical released
2. Whether it is known to be acutely toxic
3. An estimate of the quantity of the chemical released into the environment
4. The time and duration of the release
5. Where the chemical was released (e.g., air, water, and land)
6. Known health risks and necessary medical attention that will be required
7. Proper precautions, such as evacuation
8. The name and telephone number of the contact person at the plant or facility at which the release occurred

As soon as is practical after the release, there must be a written follow-up emergency notice, updating the initial information and giving additional information on response actions already taken, known or anticipated health risks, and advice on medical attention. Law has required the reporting and written notices since 1986.

6.8 Plan Implementation

Once an emergency plan has been developed, its successful implementation can be assured only through constant review and revision. Helpful ongoing procedures are

1. Routine checks of equipment inventory, status of personnel, status of hazards, and population densities
2. Auditing of the emergency procedures
3. Routine training exercises
4. Practice drills

The emergency coordinator must assure that the emergency equipment is always in readiness. Siting the control center and locating its equipment is also the coordinator's responsibility. There should be both a main control center and an alternate one, in carefully chosen locations. The following items should be present at the control center:

1. Copies of the current emergency plan
2. Maps and diagrams of the area
3. Names and addresses of key functional personnel
4. Means to initiate alarm signals in the event of a power outage
5. Communication equipment (e.g., phones, radio, TV, and two-way radios)
6. Emergency generators and lights
7. Evacuation routes detailed on the area map
8. Self-contained breathing equipment for possible use by the control center crew
9. Miscellaneous furniture, including cots

Inspection of emergency equipment such as fire trucks, police cars, medical vehicles, personal safety equipment, and alarms should be performed routinely.

The plan should be audited on a regular basis, at least annually, to ensure that it is current. Items to be updated include the list of potential hazards and emergency procedures (adapted to any newly developed technology). A guideline for auditing the emergency response plan, adapted from literature published by the Chemical Manufacturers Association, is presented in question format as follows [11].

6.8.1 General Questions

1. What types of emergency have occurred since the last audit?
2. Are all potential emergency types covered by the plan?
3. Who is responsible for maintaining the written plan?
4. Who is authorized to activate the plan?
5. When was the last revision?

6.8.2 Emergency Organization

1. Does the plan have an organization chart that defines responsibilities?
2. Who has overall responsibility?
3. Who is responsible for each of the emergency teams (e.g., fire, police, and rescue)?
4. Who directs emergency activities in the field?
5. Are the key responsible positions covered during off hours?

6.8.3 Emergency Action

1. Will the emergency action contain the incident (e.g., reduce a toxic cloud and contain a spill)?
2. Will the emergency action harm the environment?
3. Is evacuation the only alternative listed?
4. Could the emergency action be improved?

6.8.4 Alarms

1. How is the alarm activated?
2. What provisions are made for an alarm during a power failure?
3. Can all affected people hear the alarm or see the designated signal?
4. If the alarm is activated, what actions are taken?
5. How does the alarm differentiate among emergency types?
6. How are key coordinators notified during off hours?
7. What maintenance and testing is done on the alarm system?

6.8.5 Communications

1. Who handles communications with the media and public officials?
2. Who arranges and maintains the communication equipment?
3. Who has access to special phone numbers?
4. What instructions do people have for use of phones in an emergency?
5. What radio channels are available?
6. What procedures exist for messengers?

6.8.6 Evacuation

1. Where are the people moved to?
2. Where are the alternate locations?
3. Are the evacuation signals clear?
4. Are the evacuation routes clearly marked and passable?

6.8.7 Accounting for Personnel

1. Who maintains records of people?
2. Who coordinates head counts?
3. Who keeps track of injuries and fatalities?
4. How are visitors provided for?

6.8.8 First Aid

1. Where are the stations?
2. Who is responsible for rescue?
3. Who is responsible for treatment of the injured?
4. What ambulance service is available?
5. How is the emergency coordinator advised of the status of injured persons?
6. How is training for emergency and special hazards accomplished?

6.8.9 Transportation

1. What provisions have been made for moving the injured or disabled?
2. What provisions have been made for transporting fire, police, and rescue squads?
3. What provisions have been made for transporting medical supplies?
4. Who is responsible for assembling vehicles at designated spots?

6.8.10 Security

1. Who controls the emergency perimeter?
2. Are these people protected?
3. Who is responsible for training them?

6.8.11 Firefighting

1. Who maintains the equipment?
2. Who does the training?
3. How are firefighters notified when an emergency occurs?

6.8.12 Outside Agencies

1. Who decides when to alert them?
2. Who actually alerts them?

6.8.13 Training

1. Who handles training of all emergency personnel?
2. Who gives the public awareness training?
3. Who briefs the media?
4. Are local officials kept informed?
5. How is the training evaluated?
6. How often is training done?

Additional details are provided throughout earlier sections of this chapter.

Certain operational aspects of the plan should be practiced to assure that the proper response will be realized if and when an actual emergency occurs. The drill scenario should be prepared almost as carefully as the emergency plan itself. Both preannounced and surprise drills should be held, observed, and evaluated to pinpoint deficiencies in the plan and to determine whether new training is required. The following questions should be used in evaluating drills.

1. What kinds of drills are performed?
2. What aspects are tested?
3. How often are the drills held?
4. Are there both announced and unannounced drills?
5. Comparing response times for announced and unannounced drills, are times for unannounced drills much longer?
6. What time of the day are the drills held?
7. Who is responsible for evaluating the drill?

Once deficiencies have been identified, the plan should be revised to correct them. Such testing and revision should be done regularly; the interval between tests and revisions should not exceed 1 year.

For the interested reader, further information on emergency planning and response is available in Refs. [12–28].

6.9 Other State Regulatory Initiatives

In addition to the rules, regulations, and procedures provided earlier for emergency planning and response, each state (in the United States) is actually involved in other environmental management activities. Matystik et al. [29] have prepared a summary outline for interested users on these other state regulatory initiatives. The outline is a “baker’s dozen” of information which include the following for each state:

1. Agency name (which varies widely)
2. Acronym
3. URL for the environmental agency home page
4. Date the website was last updated, if listed on the agency’s home page
5. A general description of the agency
6. A contact for each agency with e-mail, phone, fax, and information where available

7. Main office, mailing address, street address, e-mail, phone, and fax along with information on other offices. (*Note:* Other contacts and e-mail addresses were listed in various tables are for the primary contact for that division [if available] or for the division or agency head [if unavailable]. In some cases, the e-mail address may be general [nonpersonal] or it may be the e-mail address of another person designated by the agency as the contact. E-mail links were randomly tested, but in many cases one cannot determine whether a non-functional address may have been incorrectly listed by the agency or if there was a system problem when tested. In cases where any "mail to" links are found to be inoperable, the reader is encouraged to resend the inquiry to the agency director's office requesting that it be forwarded appropriately.)
8. Basic descriptions of three major environmental areas: air, water, and solid/hazardous waste/land; contacts; permits and file downloads (for each area when available)
9. Basic laws of the three major environmental areas
10. Online laws, rules, and regulations, i.e., links to specific state laws, rules, and regulations
11. The availability of downloadable forms, files, permits, and publications with the URL for the download area and information on the formats used to determine if one will require any special software, such as Adobe Acrobat™ Reader for ".pdf" files, Microsoft Word™ for ".doc" files, etc.
12. Specialized information on pollution prevention
13. Special features of a particular state's website, with positives and negatives

6.9.1 New Jersey Toxic Catastrophe Prevention Act

Perhaps, the only state that has truly addressed catastrophic accidents is New Jersey. Two important features of the aforementioned act are as follows:

1. The act is applicable (registration is required) to plants handling, using, manufacturing, storing, or having the capability to generate any "extraordinarily hazardous substances" (defined by NJDEP) in at least "registration quantity."
2. These plants must have an acceptable "risk management program" in place or undertake an "extraordinarily hazardous substance accident risk assessment."

New Jersey also detailed what constituted as Acceptable Risk Management Program (RMP). This includes

1. At least one safety review report prepared in the last 2 years
2. At least one hazard analysis report with risk assessment, where required, prepared in the last 4 years
3. Hazard Analysis Report—Hazard and Operability Study (HAZOP), failure mode and effect analysis, quantitative fault tree analysis, or what/if check list (see Chapter 14 for details on these subjects)

The New Jersey Toxic Catastrophe Prevention Act (TCPA) defined an RMP through which a registered facility had to demonstrate to the department how it handled the risks associated with using EHSs. The RMP is the heart of the TCPA program. The following are the minimum eight elements of an RMP as defined by the TCPA:

1. *Safety review*: to ensure that the EHS facility is operated as designed, that no unauthorized modifications were performed, and that new facilities and modifications are designed according to state-of-the-art technology
2. *Standard operating procedures*: to ensure that approved procedures covering all aspects of the handling of an EHS are in place for the appropriate operators
3. *Preventive maintenance program*: to ensure that EHS equipment is routinely tested and inspected and only authorized modifications are performed
4. *Operator training program*: to establish the critical initial training for anyone handling an EHS at the facility and provide annual refresher training
5. *Accident investigation procedures*: to evaluate any EHS accidents that occur, with the focus on prevention of a recurrence
6. *Risk assessment*: to identify the risk of an EHS accident associated with a particular EHS operation and, if required, determine the likelihood and consequences of the accidental release in order to develop a risk reduction plan that focuses on accident prevention
7. *Emergency response program (ERP)*: to develop a response plan to be implemented in the event of an EHS accident
8. *Audit procedures*: to ensure that all RMP elements are being implemented

Civil administrative penalties for each violation were initially set at

- \$10,000 for the first offense
- \$20,000 for the second offense
- \$50,000 for the third offense

6.10 Illustrative Examples

Illustrative Example 6.1

Although this chapter addresses emergency response planning from an industrial perspective, explain why it would be advantageous to also explore emergency response planning at the home or office.

Solution

1. Keep stairs clear of debris. The same applies at a plant. This is a safety and accident concern.
2. Install fire/smoke detectors. This is a safety and accident concern.
3. Keep the house well ventilated. The same applies to the enclosed area of a plant. This is a health concern.

Illustrative Example 6.2

Briefly describe the different types of emergencies.

Solution

1. Natural: tornadoes, hurricanes, windstorms, earthquakes, avalanches, dust or sand storms, whiteouts, floods, etc.
2. Fires and explosions
3. System failures: runaway reactions, vessel and/or pipe rupture, spills, sudden releases of hazardous/toxic chemicals, power/utility failures, and radiation leaks
4. Traffic/transportation: derailments, overturned tanker trucks, accidents at sea, and oil spills
5. Human behavior: riots, sabotage, strikes, work stoppages, and crowds
6. Military action in wartime

Illustrative Example 6.3

What are some of the priorities in emergencies?

Solution

1. Protecting public safety: evacuation; rescue; and care of employees, customers, visitors, and general public
2. Protecting property: cut power and shut down of process equipment and reactors
3. Cleanup and salvage: spills, repairable equipment, etc.
4. Restoring normal operations: check for safety before start-up

Illustrative Example 6.4

What are the reasons to plan before an emergency strikes?

Solution

The primary reasons for emergency planning are as follows:

1. To minimize the effects of a disaster, the loss of life, and property damage
2. To respond immediately. Because it is sometimes difficult to think clearly during an emergency situation, responses must be learned first to act quickly later
3. To minimize “chemophobia”
4. To reduce the chance of an improper response, which can make the situation worse
5. To meet the requirements of the SARA for communities to develop emergency response plans and planning committees
6. To respond to the fact that accidents and emergencies will always occur; they are unavoidable and the best way to cope with them is to be prepared prior to the occurrence

Illustrative Example 6.5

Provide an overview of the EPCRA.

Solution

The EPCRA was passed in response to concerns regarding the environmental and safety hazards posed by the storage and handling of toxic chemicals. These concerns were triggered by the disaster in Bhopal, India, in which more than 2000 people suffered death or serious injury from the accidental release of methyl isocyanate. To reduce the likelihood of such a disaster in the United States, Congress imposed requirements on both states and regulated facilities.

The EPCRA established requirements for federal, state, and local governments, Native American Tribes, and industry regarding emergency planning and “Community Right-to-Know” reporting on hazardous and toxic chemicals. The Community Right-to-Know provisions helped increase the public’s knowledge and provide access to information on chemicals at individual facilities, their uses, and releases into the environment. States and communities, working with facilities, can use the information to improve chemical safety and protect public health and the environment.

The EPCRA has four major provisions, the details of which are codified in 40 CFR Part 370:

1. Emergency planning (Section 301–303)
2. Emergency release notification (Section 304)
3. Hazardous chemical storage reporting requirements (Sections 311–312)
4. Toxic chemical release inventory (Section 313)

Illustrative Example 6.6

Describe the Toxics Release Inventory (TRI) Program.

Solution

EPCRA's primary purpose is to inform communities and citizens of chemical hazards in their areas. Sections 311 and 312 of EPCRA require businesses to report the locations and quantities of chemicals stored on-site to state and local governments in order to help communities prepare to respond to chemical spills and similar emergencies. EPCRA Section 313 requires EPA and the states to annually collect data on releases and transfers of certain toxic chemicals from industrial facilities and make the data available to the public in the TRI. In 1990, Congress passed the Pollution Prevention Act that required that additional data on waste management and source reduction activities also be reported under TRI. The goal of TRI is to empower citizens, through information, to hold companies and local governments accountable in terms of how toxic chemicals are managed.

The EPA compiles the TRI data each year and makes it available through several data access tools, including the TRI Explorer and Envirofacts. There are other organizations that also make the data available to the public through their own data access tools, including Unison Institute that puts out a tool called "RTKNet" and Environmental Defense that has developed a tool called "Scorecard."

The TRI Program has expanded significantly since its inception in 1987. The EPA has issued rules to roughly double the number of chemicals included in the TRI to approximately 650. Seven new industry sectors have been added to expand coverage significantly beyond the original covered industries, i.e., manufacturing industries. Most recently, the EPA has reduced the reporting thresholds for certain persistent, bioaccumulative, and toxic (PBT) chemicals in order to be able to provide additional information to the public on these chemicals.

Illustrative Example 6.7

What four steps should be taken routinely to ensure that an emergency plan is viable?

Solution

1. Check inventory of equipment, personnel, hazards, and population densities on a routine basis; check readiness status of control center; and assure emergency equipment is maintained and ready for immediate use
2. Audit the emergency procedures
3. Train on a routine basis
4. Carry out practice drills on a routine basis

Illustrative Example 6.8

Describe the correct way to write an emergency response plan.

Solution

There is no single right way to write a plan. The aforementioned guidance presents a comprehensive approach to planning. Small communities with few planning resources, or communities with few or no threatening hazards, can choose the planning elements appropriate to their circumstances. Every community, however, should evaluate its preparedness for responding to an incident and plan accordingly.

Illustrative Example 6.9

Provide information on personal protection equipment (PPE).

Solution

PPE may be viewed as the workers' last line of defense against injury in the workplace. When the work environment cannot be made safe by incorporating sound engineering, tried and tested work practices, and administrative controls, PPE is employed as a "last resort." PPE effectively imposes a barrier between the worker and the health or hazard problem but does not reduce or eliminate the problem. PPE includes safety goggles, helmets, face shields, gloves, safety shoes, hearing protection, full-body protective wear, and respirators.

Illustrative Example 6.10

List some of the precautions that should be taken when wearing personal protective equipment.

Solution

Protective equipment can be heavy and awkward to wear. One uses more energy and oxygen while wearing it. Thus, one should be careful not to become overexerted. Individuals should be aware of heat sickness. Heavy clothing and equipment can trap heat causing body temperature and heart rate to rise. Individuals should be sure not to get dehydrated by drinking lots of water before starting and finishing a job. Last, the air supply should be monitored since heavy protective gear and physical exertion may cause one to run out of air faster than the rated capacity.

Illustrative Example 6.11

Describe safety requirements for pressure vessels.

Solution

Pressure vessels of any type require safeguards in order to protect personnel against their accidental failure. The American Society of Mechanical Engineers (ASME) publishes specific standard requirements for safety devices, instrumentation, and controls. Chemical process equipment should include overpressure relief devices, including safety

relief valves and rupture discs, where necessary. Provisions should be made to ensure that the contents of the vessel are not released into areas where personnel are put at risk and placed in danger.

Illustrative Example 6.12

In an emergency, what methods can be used to notify the public? What methods could be used if the emergency includes a power failure?

Solution

The following methods can be used to notify the public in case of an emergency:

1. The sounding of fire alarms in different ways to indicate certain kinds of emergencies
2. Chain phone calls (this method usually works well in small towns)
3. Police cars or volunteer teams with loudspeakers or bullhorns
4. Radio and television; emergency signals followed by official instructions
5. House-to-house notification through the use of the National Guard and/or Armed Forces

In the event of a power failure, the following means could be employed:

1. Police cars or volunteer teams with loudspeakers or bullhorns
2. Radio communications that are accessed through battery operated or car radios
3. House-to-house notification through the use of the National Guard and/or Armed Forces

Illustrative Example 6.13

Discuss the Occupational Safety and Health Administration (OSHA) involvement with emergency planning and response. (OSHA is discussed in Chapter 5.)

Solution

1. OSHA requires that all facilities establish accident prevention and safety programs. The program is designed to minimize accidents associated with the workplace.
2. Facilities that use and/or store a hazardous chemical must submit material safety data sheets (MSDSs) (see Illustrative Example 6.14) to OSHA and all other required agencies to track chemicals at the facility and to establish an emergency plan in the event of a release.
3. Training is required on accident prevention and response for all employees at a facility.

Illustrative Example 6.14

What information should an MSDS contain?

Solution

The MSDS should contain the following:

1. Identity of chemical
2. Identity of ingredients in a hazardous chemical mixture
3. Chemical and physical characteristics of the chemical
4. Chemical and physical hazards of the chemical
5. Acute and chronic health problems, including signs and symptoms of exposure and medical conditions
6. Primary route of entry
7. Personal exposure limits in terms of maximum duration and concentration
8. Protective measures and special precautions
9. Emergency procedures and first aid procedures
10. Date of preparation of the MSDS
11. Identification of that individual or group or agency responsible for the information contained on the MSDS

The reader is referred to Section 8.5 and Illustrative Examples 8.9 through 8.13 for additional information.

Illustrative Example 6.15

A chemical reactor at a plant site has exploded. Provide specific steps for coping with this accident/emergency.

Solution

1. Check if anyone is hurt
2. Check if another explosion may occur
3. Leave the accident if necessary
4. Call 911 as soon as possible
5. Notify as many people as possible

Illustrative Example 6.16

In 1947, two ships docked in Texas City, Texas, with tons of ammonium nitrate fertilizer and other cargo aboard. These ships caught fire, burned, and exploded over a period of more than 16h. The explosions were so powerful that almost 600 people were killed and more than 3500 people were injured. That area and much of the city was destroyed. One of the ship's anchors was thrown approximately 2 miles inland where it still lies today as a memorial to the incident (see also Chapter 3).

As described earlier, the EPCRA, among other things, requires any facility that produces, uses, or stores any chemical on a published list in excess of the "threshold planning quantity" to notify local emergency

response entities (such as the fire department, police department, hospitals, etc.) of the quantity, identity, and nature of these chemicals; to cooperate with an LEPC; and to develop an emergency plan to be used in the event of a release.

While the regulatory definition of a “facility” includes transportation vessels and port authorities for release reporting, these entities are exempt from notification and emergency planning requirements. As a result, emergency response planning against another Texas City disaster is not a requirement of the EPCRA legislation.

Prepare a list of areas of concern that would have to be addressed if the notification and emergency planning requirements were applied to port areas. Among other things, you may wish to address matters such as the short residence time of in-transit materials and the political (as opposed to legal) ramifications of applying regulation of this kind to foreign flag carriers. *Note:* This is an open-ended question with many correct answers. Additional examples/problems of this type are available in Ref. [30].

Solution

The following issues should be addressed in the notification and emergency planning for port areas:

1. Who shall be responsible for notification and/or emergency planning—the shipper, transporter, or port operator?
2. How shall the inventory of the materials flowing in and out of the area be maintained?
3. Should there be a minimum storage time that triggers notification and emergency planning?
4. Should an emergency plan be developed for the release of every chemical that ever flowed through the port even though some of those chemicals may never be present in the area again?
5. What notification and emergency planning criteria should be adopted for large quantities of listed materials that frequently flow through the port but are present for only short periods of time?
6. Should limits be placed on quantities of some materials being stored in the port area at a given time?
7. Should ports be classified as to what materials are allowed to enter them?
8. Should segregation of cargo by compatibility groups be required for materials waiting to be loaded or transshipped?
9. Should port areas be rezoned to reduce the potential risk to the surrounding population?
10. Are evacuation plans possible for port areas in large cities?
11. Is there sufficient authority under current law to accomplish this task or is new legislation required?
12. What would be the political consequences of requiring foreign ships to adhere to these regulations?
13. What would be the cost of applying these regulations to port areas?

Illustrative Example 6.17

Describe how the ERP works with respect to oil spills.

Solution

When a spill (or release) occurs, the company responsible for the release, its response contractors, the local fire and police departments, and the local emergency response personnel provide the first line of defense. If needed, a variety of state agencies stand ready to support, assist, or take over response operations if an incident is beyond local capabilities. In cases where a local government or Native American tribe conducts temporary emergency measures in response to a hazardous substance release but does not have emergency response funds budgeted, the EPA operates a Local Governments Reimbursement program that will reimburse local governments or Native American tribes up to \$25,000 per incident.

If the amount of oil spilled exceeds the established reporting trigger, the organization responsible for the release or spill is required by law to notify the federal government's National Response Center (NRC). Once a report is made, the NRC immediately notifies a predesignated EPA or U.S. Coast Guard On-Scene Coordinator (OSC) based on the location of the spill. The procedure for determining the lead agency is clearly defined, so there is no confusion about who is in charge during a response. The OSC determines the status of the local response and monitors the situation to determine whether, or how much, federal involvement is necessary. It is the OSC's job to ensure that the cleanup, whether accomplished by industry, local, state, or federal officials, is appropriate, timely, and minimizes human and environmental damage.

The OSC may determine that the local action is sufficient and that no additional federal action is required. If the incident is large or complex, the federal OSC may remain on the scene to monitor the response and advise on the deployment of personnel and equipment. However, the federal OSC will take command of the response in the following situations:

1. If the party responsible for the chemical release or oil spill is unknown or is not cooperative
2. If the OSC determines that the spill or release is beyond the capacity of the company, local, or state responders to manage
3. For oil spills, if the incident is determined to present a substantial threat to public health or welfare due to the size or character of the spill

The OSC may request additional support to respond to a release or spill, such as additional contractors, technical support from EPA's Environmental Response Team, or Scientific Support Coordinators from the EPA or the National Oceanic and Atmospheric Administration. The OSC also may seek support from the Regional Response Team (RRT) to access special expertise or to provide additional logistical support. In addition, the National Response Team (NRT) stands ready to provide

backup policy and logistical support to the OSC and the NRT during an incident.

The federal government will remain involved at the oil spill site following response actions to undertake a number of activities, including assessing damages, supporting restoration efforts, recovering response costs from the parties responsible for the spill, and, if necessary, enforcing the liability and penalty provisions of the Clean Water Act, as amended by the Oil Pollution Act of 1990. See Section 5.8 for more details on the OPA and aspects of the OPA liability and cost recovery provisions that are currently under review in response to the 2010 BP Deepwater Horizon offshore oil rig explosion.

The reader is also referred to the literature for examples/problems of this nature at <http://www.epa.gov/superfund/programs/er/nrs works.htm>

Illustrative Example 6.18

Who was it that once said “an ounce of prevention is worth a pound of cure”?

Solution

The answer can be found in the Afterword on page 591.

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Part II

Health Risk Assessment

When an epidemic of physical disease starts to spread, the community approves and joins in quarantine of the patients in order to protect the health of the community against the spread of the disease ...

Franklin Delano Roosevelt (1882–1945)

Speech at Chicago, October 5, 1937

7

Introduction to Health Risk Assessment

7.1 Introduction

As noted in Part I, there are many definitions of the word “risk”. Some of the definitions provided are as follows: it is a combination of uncertainty and damage; a ratio of hazards to safeguards; a triplet combination of event, probability, and consequences; or even a measure of economic loss or human injury in terms of both the incident likelihood and the magnitude of the loss or injury.

People face all kinds of risks everyday, some voluntarily and others involuntarily. Therefore, risk plays a very important role in today’s world. Studies on cancer caused a turning point in the world of risk because it opened the eyes of risk scientists and health professionals to the world of health risk assessments (HRAs).

The usual objective of HRA and the accompanying calculations is to evaluate the potential for adverse health effects from the release of chemicals into the environment. Unfortunately, the environment is very complex since there is a vast array of potential receptors present. The task of testing and evaluating all of the enormous number of chemicals on the market for their impact on human populations and ecosystems becomes extremely difficult. To further complicate the problem, health is a concept that has come to mean different things to different people. Some have defined it as follows: “... a state of complete physical, mental and social well-being and not merely the absence of disease or infirmity.” Many other definitions and concepts have been purposed and appear in the literature.

Since 1970, the field of HRA has received widespread attention within both the scientific and the regulatory communities. It has also attracted the attention of the public. Properly conducted risk assessments and risk assessment calculations have received fairly broad acceptance, in part because they put into perspective the terms toxic, health, hazard, and risk. Toxicity is an inherent property of all substances. It states that all chemical and physical agents can produce adverse health effects at some dose or under some specific exposure conditions. In contrast, exposure to a chemical that has the capacity

to produce a particular type of adverse effect represents a health “hazard.” Risk (in a general sense), however, is the probability or likelihood that an adverse outcome will occur in a person or a group that is exposed to a particular concentration or dose of the hazardous agent. Health risk is therefore a function of exposure and dose. Consequently, HRA is defined as the process or procedure used to estimate the likelihood that humans or ecological systems will be adversely affected by a chemical or physical agent under a specific set of conditions.

The term risk assessment is not only used to describe the likelihood of an adverse response to a chemical or physical agent, but it has also been used to describe the likelihood of any unwanted event. These include risks such as explosions or injuries in the workplace; natural catastrophes; injury or death due to various voluntary activities such as skiing, sky diving, flying, and bungee jumping; diseases; death due to natural causes; and many others [1]. These other risk scenarios are treated in more detail in Part III.

Risk assessment and risk management are two different processes, but they are intertwined. Risk assessment and risk management give a framework not only for setting regulatory priorities but also for making decisions that cut across different environmental areas. Risk management refers to a decision-making process that involves such considerations as risk assessment, technology feasibility, economic information about costs and benefits, statutory requirements, public concerns, and other factors. Therefore, risk assessment supports risk management in that the choices on whether and how much to control future exposure to a suspected problem may be determined during the risk management process [2]. Regarding both risk assessment and risk management, this chapter and the four chapters to follow will primarily address this subject from a *health* perspective.

Corporations that manufacture, sell, and purchase chemicals now realize that the chemicals they handle present health risks to their employees, their customers, and/or to the public. The assessment process is often an enormous task since the health risks of scores of chemicals may have to be assessed from a risk perspective. As noted in Chapter 4, each individual HRA is a multistep process consisting of:

1. Health problem identification
2. Toxicological concerns
3. Exposure characterization
4. Risk characterization

This is often followed by an analysis of the results and (perhaps) risk management.

Before concluding this section, the reader is again reminded of the differences between HRA and hazard risk assessment (HZRA). Unfortunately, both terms have been used interchangeably by researchers and industrial

personnel. As indicated earlier, this part of the book addresses chronic health problems (HRA), while Part III will be primarily focused on acute hazard problems (HZRA).

7.2 Health Risk Evaluation Process

HRAs provide an orderly, explicit, and consistent way to deal with issues in evaluating whether a health problem exists and what the magnitude of the problem may be. This evaluation typically involves large uncertainties because the available scientific data are limited, and the mechanisms for adverse health impacts or environmental damage are only imperfectly understood.

When one examines risk, how does one decide how safe is safe, or how clean is clean? To begin with, one has to look at both inputs of the risk equation, i.e., both the toxicity of a pollutant and the extent of exposure. Information is required for both the current and the potential exposure, considering all possible exposure pathways. In addition to human health risks, one needs to look at potential ecological or other environmental effects. In conducting a comprehensive HRA, one should remember that there are always uncertainties, and these uncertainties must be included in the analysis [2].

In recent years, several guidelines and handbooks have been published to help explain approaches for conducting HRAs. As discussed by a special National Academy of Sciences committee convened in 1983, most human or environmental health hazards can be evaluated by dividing the analysis into four parts: health problem identification, dose–response assessment or toxicity assessment, exposure assessment, and risk characterization (see Figure 7.1). This is an expansion of the HRA figure presented in Chapter 4. For some perceived health problems, the risk assessment might stop with the first step, health problem identification, if no adverse effect is identified or if an agency elects to take regulatory action without further analysis [1]. Regarding identification, a health problem is defined as a toxic agent or a set of conditions that has the potential to cause adverse effects to human health or the environment. Health problem identification involves an evaluation of various forms of information in order to identify the different problems. Dose–response or toxicity assessment is required in an overall assessment; responses/effects can vary widely since all chemicals and contaminants vary in their capacity to cause adverse effects. This step frequently requires that assumptions be made to relate experimental results from animal tests to expected effects on exposed humans. Exposure assessment is the determination of the magnitude, frequency, duration, and routes of exposure of toxic agents to human populations and ecosystems. Finally, in health risk

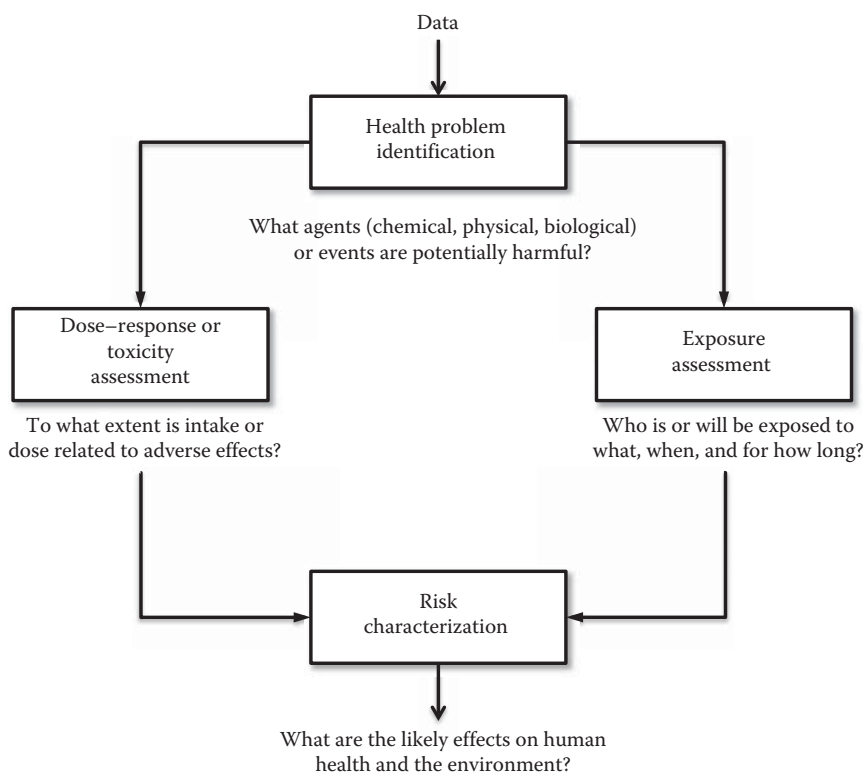


FIGURE 7.1
Health risk evaluation process.

characterization, toxicology and exposure data/information are combined to obtain a qualitative or quantitative expression of risk.

HRA involves the integration of the information and analysis associated with the aforementioned four steps to provide a complete characterization of the nature and magnitude of risk and the degree of confidence associated with this characterization. A critical component of the assessment is a full elucidation of the *uncertainties* associated with each of the major steps. Under this broad concept of risk assessment are encompassed all of the essential problems of toxicology. Risk assessment takes into account all of the available dose-response data. It should treat uncertainty not by the application of arbitrary safety factors but by stating them in quantitatively and qualitatively explicit terms, so that they are not hidden from decision makers. Risk assessment defined in this broad way forces a risk assessor to confront all the scientific uncertainties and to set forth in explicit terms the means used in specific cases to deal with these uncertainties [3]. An expanded presentation on each of the four HRA steps is provided below. The reader may choose to refer to Chapter 4 for an abbreviated introduction to these topics.

7.3 Health Problem Identification

Health problem identification is the most easily recognized of the actions required of risk managers or regulatory agencies. It is defined as the process of determining whether human exposure to an agent could cause an increase in the incidence of an adverse health condition (cancer, birth defect, etc.) or whether exposure to a nonhuman receptor, e.g., fish, birds, or other wildlife, might cause adverse effects. It involves characterizing the nature and strength of the evidence of causation. Although the question of whether a substance causes cancer or other adverse health effects in humans is theoretically a yes/no question, there are few chemicals or physical agents on which the human data are definitive. Therefore, the question is often restated in terms of effects in laboratory animals or other test systems: "Does the agent induce cancer in test animals?" Positive answers to such questions are typically taken as evidence that an agent *may* pose a cancer risk for any exposed human. Information for short-term *in vitro* tests and structural similarity to known chemicals may, in certain circumstances, also be considered as adequate information for identifying a health problem [1].

A health problem identification effort for a chemical plant or industrial application can include information about:

1. Chemical inventories
2. The locations of facilities that use, produce, process, or store chemical materials that can be classified as health problems
3. The design of the chemical plant
4. The quantity of material that is normally involved in a release
5. The nature of the problem most likely to accompany the health problem

An important aspect of problem identification is a description of the pervasiveness of the problem. For example, most environmental assessments require knowledge of the concentration of material in the environment, weighted in some way to account for the geographical magnitude of the site affected, e.g., a 1 or 300 acre site, a 1,000 or 1,000,000 gal/min stream, etc. All too often environmental incidents regarding chemical emission have been described by statements like "concentrations as high as 150 ppm of a chemical were measured at a 1,000 acre waste site." However, on closer examination, one may find that only 1 of 200 samples collected on a 20 acre portion of a 1,000 acre site showed this concentration and that 2 ppm was the geometric mean concentration of contamination in the 200 samples.

An appropriate sampling program is critical in the conduct of an HRA. This topic could arguably be part of the exposure assessment, but it has been placed within the identification step because, if the degree of contamination

is small, no further work may be necessary. Not only is it important that samples be collected in a random or representative manner, but the number of samples must also be sufficient to conduct a statistically valid analysis. The number needed to insure statistical validity will be dictated by the variability among the results. The larger the variance, the greater the number of samples needed to define the problem [1].

As noted, the means of identifying health problems is complex. Different methods are used to collect and evaluate a chemical's toxic properties (those properties that indicate the potential to cause biological injury, disease, or death under certain exposure conditions). One method is the use of *epidemiological* studies that deal with the incidence of disease among groups of people following exposure to the toxic agent under consideration. Epidemiological studies attempt to correlate the incidence of a given adverse effect from an emission by an evaluation of people with a particular adverse effect and people without it. Long-term animal bioassays are the most common method of determination. (A bioassay is referred to here as an evaluation of disease in a laboratory animal.) Increased tumor incidence in laboratory animals is the primary health effect considered in animal bioassays when evaluating carcinogenicity (the development of cancer). Exposure testing for a major portion of an animal's lifetime (2–3 years for rats and mice) provides information on disease and susceptibility related to a chemical's carcinogenicity.

The understanding of how a substance is handled in the body, transported, changed, and excreted, and of the response of both animals and humans to it, has advanced remarkably in the last few decades. There are, however, many questions that remain concerning these animal tests as to what information they provide, which kinds of studies are the best, and how the animal data compare with human data. In an attempt to answer these questions, epidemiological studies and animal bioassays are then compared to each other to determine if a particular chemical is likely to pose a health problem to humans based on results of animal tests. Many assumptions are made in these assessments. For example, it is assumed that the chemical administered in a bioassay is in a form similar to that present in the environment. Another assumption is that animal carcinogens are also human carcinogens. An example is that there is a similarity between animal and human metabolism, and so on. Lists of hazardous chemicals have been developed [2] based on these and other assumptions.

An expanded discussion of this topic follows in the next chapter.

7.4 Toxicology and Dose–Response

Dose–response assessment is the process of characterizing the relationship between the dose of an agent administered or received and the incidence of

an adverse health effect in exposed populations, as well as estimating the incidence of the effect as a function of exposure to the agent. This process considers such important factors as intensity of exposure, age, pattern of exposure, and other variables that might affect response, such as sex, lifestyle, and other modifying factors. A dose–response assessment usually requires extrapolation from high to low doses and extrapolation from animals to humans or from one laboratory animal species to a wildlife species. A dose–response assessment should describe and justify the methods of extrapolation used to predict incidence, and it should characterize the statistical and biological uncertainties in these methods. When possible, the uncertainties should be described numerically rather than qualitatively.

Toxicologists tend to focus their attention primarily on extrapolations from cancer bioassays. However, there is also a need to evaluate noncancer effects of lower doses on various organs and systems in the body. Many scientific papers focus on the use of a safety factor or uncertainty factor approach since all adverse effects other than cancer and mutation-based developmental effects are believed to have a threshold concentration, i.e., a dose below which no adverse effect should occur. Several researchers have discussed various approaches to setting acceptable daily intakes or exposure limits for developmental and reproductive toxicants. It was originally thought that an acceptable limit of exposure could be determined using cancer models, but today they are considered inappropriate because of thresholds for noncancer effects [1].

For a variety of reasons, it is also difficult to precisely evaluate toxic responses caused by acute exposures to hazardous materials. First, humans experience a wide range of acute adverse health effects, including irritation, narcosis, asphyxiation, sensitization, blindness, organ system damage, and death. In addition, the severity of many of these effects varies with intensity and duration of exposure. Second, there is a high degree of variation in response among individuals in a typical population. Third, for the overwhelming majority of substances encountered in industry, there are not enough data on toxic responses of humans to permit an accurate or precise assessment of the substance's health problem potential. Fourth, many releases involve multicontaminants. There are presently no rules on how these types of releases should be evaluated, i.e., chemicals acting synergistically, antagonistically, or no interaction at all. Fifth, there are no toxicology testing protocols that exist for studying episodic exposures to animals. In general, this has been a neglected area of toxicology research. There are many useful measures available for benchmarking the predicted likelihood that a release event will result in serious injury or death. Several references review various toxic effects and discuss the use of various established toxicological criteria [4–6].

Dangers are not necessarily defined by the presence of a particular chemical, but rather by the amount of that chemical one is exposed to, also known as the dose. A dose is usually expressed in milligrams of chemical

received per kilogram of body weight per day. For toxic substances other than carcinogens, a threshold dose must be exceeded before a health effect occurs, and, for many substances, there is a dosage below which there is no harm. A health effect will occur or at least be detected at the threshold. For carcinogens, it is assumed that there is *no* threshold, and, therefore, any substance that produces cancer is assumed to produce cancer at *any* concentration. It is vital to establish the link to cancer and to determine if that risk is acceptable. Analyses of cancer risks are much more complex than noncancer risks [2].

Not all contaminants or chemicals are created equal in their capacity to cause adverse effects. Thus, cleanup standards or action levels are usually based in part on the compounds' toxicological properties. As noted earlier, toxicity data are derived largely from animal experiments in which the animals (primarily mice and rats) are exposed to increasingly higher concentrations or doses. Responses or effects can vary widely from no observable effects to temporary and reversible effects, to permanent injury to organs, to chronic functional impairment, to, ultimately, death.

An expanded presentation of this topic can be found in Chapter 9.

7.5 Exposure Assessment

Exposure assessment is the process of measuring or estimating the intensity, frequency, and duration of human or animal exposure to an agent currently present in the environment or of estimating hypothetical exposures that might arise from the release of new chemicals into the environment. In its most complete form, an exposure assessment should describe the magnitude, duration, schedule, and route of exposure; the size, nature, and classes of the human, animal, aquatic, or wildlife populations exposed; and the uncertainties in all estimates. The exposure assessment can often be used to identify feasible protective control options and to predict the effects of available control technologies for controlling or limiting exposure [1].

Much attention has recently been focused on exposure assessment because many of the risk assessments performed in the past used too many conservative assumptions, which, in turn, caused an overestimation of the actual exposure. Obviously, without exposures there are no risks. To experience adverse effects, one must first come into contact with the toxic agent(s).

Generally, the main pathways of exposure considered in this step are via the atmosphere, by inhalation of air during breathing, by ingestion of surface and groundwater, by ingestion of toxic materials that have passed through the aquatic and terrestrial food chain, and through the skin via dermal absorption. Once an exposure assessment determines the quantity of a chemical with which human populations may come in contact, the information can

be combined with toxicity data (from the dose–response step) to estimate potential health risks [2]. The primary purpose of an exposure assessment is to determine the concentration levels over time and space in each environmental media where human and other environmental receptors may come into contact with chemicals of concern. There are four major components of an exposure assessment: (1) potential sources, (2) significant exposure pathways, (3) populations potentially at risk, and (4) exposure estimates.

The two primary methods of determining the concentration of a pollutant to which target populations are exposed are via direct measurement and computer analysis (also known as computer modeling). Measurement of the pollutant concentration in the environment is used for determining the risk associated with an existing source. Receptors are placed at regular intervals from the source, and the concentration of the pollutant is measured over a certain period of time (usually several months or a year). The results are then related to the size of the local population. This kind of monitoring, however, is expensive and time-consuming. Many measurements must be taken because exposure levels can vary under different environmental conditions or at different times of the year. Computer fate and transport modeling predicts environmental concentrations of pollutants (see Chapter 10 for more information on dispersion modeling). In the prediction of exposure, computer modeling focuses on the discharge of a pollutant and the dispersion and possibly degradation of that pollutant by the time it reaches the receptor. This method is primarily used for assessing risk from a proposed facility or discharge. Sophisticated techniques are employed to relate reported or measured emissions to atmospheric, climatological, demographic, geographic, and other data in order to predict a population's potential exposure to a given chemical [2].

Additional details regarding exposure assessment and prediction are provided in Chapter 10.

7.6 Health Risk Characterization

Risk characterization (the fourth and final step of the HRA process) is the process of estimating the incidence of a health effect under the various conditions of human or animal exposure described in the exposure assessment. It is performed by *combining* the exposure assessment and the dose–response assessment. The summary effects of the uncertainties in the preceding steps should be described in this step. The quantitative estimate of the risk is the principal interest to the regulatory agency or risk manager making the decision. The risk manager must consider the results of the risk characterization when evaluating the economics, societal aspects, and various benefits of the risk assessment. Factors such as societal pressure, technical uncertainties,

and severity of the potential health hazard influence how the decision makers respond to the risk assessment. There is room for significant improvement in this step of the risk assessment process [1,6].

A risk estimate indicates the likelihood of occurrence of the different types of health or environmental effects in exposed populations. Risk assessments may include both human health and environmental evaluations (i.e., impacts on ecosystems). Ecological impacts include actual or potential effects on plants and animals (other than domesticated species). The number produced from the risk characterization, representing the probability of adverse health effects being caused, must be evaluated. This is performed because certain agencies will only look at specific levels of risks before they act on them.

There are two major types of risk (see Chapter 1): maximum individual risk and population/societal risk. Maximum individual risk is defined exactly as it implies, i.e., the maximum risk to an individual. This individual is usually considered to have a 70 year lifetime of exposure to a process or a chemical. Population/societal risk is the risk to an entire population. It is expressed as a certain number of deaths per thousand or per million people. For example, a fatal annual risk of 2×10^{-6} refers to two deaths per year for every million exposed individuals.

This last topic receives extensive treatment in Chapter 11.

Illustrative Example 7.1

What are the general duties of state, territorial, and local air pollution control agencies as they relate to HRAs?

Solution

The reader is referred to the following references:

1. Author unknown, *Air Pollution Information Activities at State and Local Agencies— United States*, 1992, USEPA, Washington, DC, 1994.
2. W. Matystik, L. Theodore, and R. Diaz, *An Internet Guide to State Regulatory Agencies*, Government Institutes, Washington, DC, 1992.

Illustrative Example 7.2

The HRA process is routinely used in setting *air* standards. Give the sequence of steps in the risk assessment process in the context of air standards.

Solution

The sequence of steps in the risk assessment process related to setting air standards are

1. Evaluation of the source
2. Quantification of the release
3. Assessment of the toxicity of the chemical
4. Calculations of atmospheric dispersion to the receptor
5. Quantification of exposure at designated receptors
6. Quantification of health effects associated with the release and subsequent exposure

Illustrative Example 7.3

What is the role of human HRA in risk management at a hazardous waste or Superfund site?

Solution

A human HRA estimates the likelihood of health problems occurring if no cleanup action were taken at the site, i.e., the site baseline human risk. To estimate the baseline risk, the following four-step process should be undertaken to determine the possible human risk that will then determine what sort of corrective action, i.e., risk management action, should be employed:

1. Health problem identification
2. Dose–response and toxicity assessment
3. Exposure assessment
4. Risk characterization

Illustrative Example 7.4

What are some of the important complications in the “identification” step of the HRA process?

Solution

The following factors should be reviewed in the identification step of a risk assessment effort:

1. The sufficiency of the epidemiological database for most chemicals
2. The nature of adverse health effects: cancer versus noncancer
3. The preponderant role of cigarette smoking and/or other high risk behavior (if applicable) affecting the overall outcome in the test population
4. Multisource, multipollutant synergistic impacts
5. The questionable validity of animal studies and short-term tests with respect to the prediction of long-term, adverse health impacts in a human population

Illustrative Example 7.5

Discuss how the dose–response/toxicological assessment step can be improved.

Solution

The greatest improvement would come in generating more meaningful and applicable data, particularly as they apply to humans. Information is required over a wide range of dose, concentration, duration, etc.

Illustrative Example 7.6

Discuss how the exposure assessment step can be improved.

Solution

Most of the exposure information is generated from models, e.g., the Pasquill–Gifford atmospheric dispersion model, plume rise equation, and estuary models. As was noted earlier and will be discussed again in Chapter 10, the calculations obtained from these models are often in error by several orders of magnitude. Improvements in these models would definitely improve the exposure assessment step.

References

1. D. Paustenbach, *The Risk Assessment of Environmental and Human Health Hazards: A Textbook of Case Studies*, John Wiley & Sons, Hoboken, NJ, 1989.
2. G. Burke, B. Singh, and L. Theodore, *Handbook of Environmental Management and Technology*, 2nd edn., John Wiley & Sons, New York, 2000.
3. J. Rodricks and R. Tardiff, *Assessment and Management of Chemical Risks*, American Chemical Society, Washington, DC, 1984.
4. D. B. Clayson, D. Krewski, and I. Munro, *Toxicological Risk Assessment*, CRC Press, Taylor & Francis Group, Boca Raton, FL, 1985.
5. V. Foa, E. Emmett, M. Maron, and A. Colombi, *Occupational and Environmental Chemical Hazards*, Ellis Horwood Limited, Chichester, U.K., 1987.
6. R. Bethea, *Incorporation of Occupational Safety and Health into Unit Operations Laboratory Courses*, NIOSH, Cincinnati, OH, 1991.

8

Health Problem Identification

8.1 Introduction

Health problem identification is defined as the process of determining whether human exposure to a chemical at some dose could cause an increase in the incidence of an adverse health condition (cancer, birth defect, etc.), or whether exposure to nonhumans, such as fish, birds, and other forms of wildlife, could cause adverse effects. In other words, does exposure to a chemical have the potential to cause harm? It involves characterizing the quality, nature, and strength of the evidence of causation. It may not give a yes/no answer; however, it is intended to provide an assessment on which to base a decision as to whether a health problem has been identified. This identification characterizes the problem in terms of the agent and dose of the agent. Since there are few hazardous chemicals or hazardous agents for which definitive exposure data in humans exist, the identifications of health hazards are often characterized by the effects of health problems on laboratory test animals or other species and test systems [1].

The source and classification of *pollutants* that can give rise to a health problem include the following:

1. Air pollutants
2. Indoor air pollutants
3. Water pollutants
4. Soil pollutants
5. Hazardous pollutants
6. Toxic pollutants

These are listed in Table 8.1. Additional details on sources and classification of pollutants and their potential health effects are available in the literature [1].

There are numerous methods available to identify the potential for chemicals to cause both adverse health conditions and significant effects on the

TABLE 8.1	
Classification and Typical Sources of Pollutants	
Air pollutants	
Ozone and carbon monoxide	
Airborne particulates	
Airborne toxics	
Sulfur dioxide	
Acid deposition	
Indoor air pollutants	
Radon	
Environmental tobacco smoke	
Asbestos	
Formaldehyde and other volatile organic compounds	
Pesticides	
Water pollutants	
Drinking water pollutants	
Critical aquatic habitat pollutants	
Surface water pollutants	
Land pollutants	
Industrial hazardous wastes	
Municipal wastes	
Mining wastes	
Radioactive wastes	
Pollutants from underground storage tanks	
Hazardous pollutants	
Toxic pollutants	

environment. These can include, but are not limited to, toxicology, epidemiology, molecular and atomic structural analysis, material safety data sheets (MSDSs), standardized mortality ratios (observed deaths/expected deaths), engineering approaches to problem solving, analysis of the fate of chemicals in the environment, and evaluation of carcinogenic versus noncarcinogenic health hazards.

The remaining sections of this chapter address the aforementioned key issues in the following order:

- Toxicology principles
- Epidemiology principles
- Molecular atomic structural analysis
- Material safety data sheet
- Engineering problem solving
- Fate of chemicals in the environment related to health problems
- Carcinogens versus noncarcinogens

Illustrative Example 8.1

Discuss how the “health problem identification” procedure can be improved.

Solution

The following factors should be reviewed to improve the overall effectiveness of a health risk assessment effort:

1. The epidemiological database for most chemicals is limited, so more collection and analysis of epidemiological data from long-term studies in humans is warranted.
2. Emphasis has been placed in the past on cancer effects, so more non-cancer effect data need to be collected.
3. Lifestyle choices greatly affect the preexisting conditions of an exposed population, and their synergistic affects on the magnitude of health problem from exposure to pollutants should be studied.
4. Multi-source, multi-pollutants often result in synergistic impacts from pollutant exposure, and should be carefully considered.

Illustrative Example 8.2

Would eating a breakfast food on a daily basis containing trace amounts of a carcinogen be classified as a health problem or a hazard problem?

Solution

In line with the approach and definitions provided in this book, this is a potentially chronic health problem, not an acute hazard problem.

Illustrative Example 8.3

List some “nonchemical” health-related problems.

Solution

Some of the more significant “nonchemical” sources of health-related problems include the following:

1. Ionizing radiation
2. Nonionizing radiation
3. Thermal stress (including cold stress)
4. Noise
5. Vibration

Illustrative Example 8.4

Define ergonomics.

Solution

Ergonomics involves the study of fitting the work/job to the individual. Ergonomics is also defined as human engineering factors. Ergonomic stress inducers include the following:

1. Lifting
2. Lowering
3. Holding (grasping)
4. Pushing
5. Reading

Ergonomics studies in the context of this chapter generally involve the application and understanding of human behavior, obstacles, limitations, etc., as they impact process engineering.

Illustrative Example 8.5

List some of the factors influencing the optimization of the relationship between the worker and the job.

Solution

Factors affecting worker job performance and representing potential ergonomic stress on the job include the following:

1. Thermal conditions, i.e., heat, cold
2. Illumination present, i.e., inadequate, glare
3. Physical and mental requirements of the job
4. Noise and vibration exposure
5. Exposure to hazardous materials, whether chronic or acute
6. Required interaction between worker and equipment, i.e., mechanical, electrical

8.2 Toxicology Principles

What makes a substance hazardous? From a regulatory standpoint, a substance is hazardous if it exhibits reactivity, corrosivity, ignitability, or toxicity. The potential effect of toxicity on living things, especially humans, has driven regulatory initiatives in hazardous waste management. A primary objective of hazardous waste management is to protect human health by reducing the risk associated with hazardous chemicals. Thus, an understanding of toxicology is needed in order to determine if a chemical substance is a health problem.

Chemical health problems yield toxic effects when hazardous chemicals enter the human body and other organisms at concentrations above

the “no effects level.” Adverse health effects become evident in both the short and long term with symptoms ranging from mild allergic reactions to death.

The general subject of toxicology deals with the adverse effects of chemical substances on living things. The science of toxicology is not a basic science like mathematics or physics. Toxicology is a relatively new discipline that continues to develop. It evolved from other sciences such as physiology, pharmacology, biochemistry, molecular biology, and epidemiology.

Many engineers and scientists do not fully understand toxicology, and their education and experiences usually do not prepare them to make intelligent toxicological evaluations. However, technical individuals with a background in toxicology can often assist in an overall health risk study with the identification of a chemical problem.

Since the fundamental mechanisms that cause toxic responses are not fully understood, toxicological findings are largely based on observations. Although some of the toxicological information relating to humans is based on human experience, the majority of this information is derived from animal experimentation.

Health effects of chemicals observed in laboratory experiments with animals are used to predict health effects of these same chemicals in humans. Extrapolation procedures account for the differences in exposure levels between laboratory animals and humans. Risk estimates may vary by an order of magnitude depending on the mathematical method used for this extrapolation. Thus, it is evident that the quantification of the toxicity of a chemical has a high degree of uncertainty associated with it. However, in most cases, the available toxicological data are sufficient to predict the risks associated with a chemical. In cases where the toxicological data for a chemical are insufficient, alternative approaches can be used to determine if the chemical is a health problem [2].

This subject will receive additional treatment in Chapter 9, where an extensive section is devoted to toxicology. Technical details and definitions are provided in that chapter.

8.3 Epidemiology Principles

Epidemiology is an important method employed in the identification of human toxicity and health problems resulting from exposure to chemicals. It is the only method that provides direct human evidence to identify toxicity and health problem in humans [3].

Epidemiology analyzes statistical data to determine the relationship between a chemical exposure and the exposed population. However, positive statistical analysis does not always translate into a causal relationship

between the chemical and its effect in humans. When a cause and effect relationship has been established, further statistical analysis helps define the upper limit of the human toxic response and the overall risk from exposure to the chemical.

Those epidemiological studies that establish a cause and effect relationship between a chemical and disease in humans, such as cancer or reproductive toxicity, have been drawn from studies of relatively small population groups exposed to high doses of the chemical. As noted by Tomatis [4], the identification of human carcinogens has occurred under conditions of exposure similar to those used in experimental carcinogenesis. (Carcinogenesis is the process that occurs when exposure to a carcinogenic chemical results in the development of a malignancy.) In experimental carcinogenesis, a limited number of experimental animals are exposed to high levels of a chemical or mixture of chemicals to increase the sensitivity of the experimental animal to produce a response.

Although valuable in its own right and in combination with other scientific methods, epidemiological information is limited. Epidemiological methods are not sensitive to increases in chemically induced disease at low exposure concentrations. This is an important limitation as most human exposures occur at low chemical concentrations. As a result, a negative relationship determined by epidemiology does not necessarily demonstrate the absence of a health problem, nor does it demonstrate the potential presence of one in the long term.

Epidemiology is useful in the detection of an increase in rare human diseases in an exposed population. However, the usefulness of epidemiology in the detection of an increase in common diseases is often limited due to the long latency period between exposure and detection of the disease. In order to detect an increase in more common diseases, such as cancers of the lung, breast, and colon, special circumstances must exist where the exposure dose or the incidence of the disease is unusually high. Control group studies involving unexposed humans provide data for epidemiological analysis to detect increases in common diseases, but these control groups may be difficult to identify if the exposure is widespread.

Illustrative Example 8.6

Do chemical companies and other industries keep track of employees' cancer and respiratory illnesses and deaths?

Solution

Many large companies do. Some companies keep extremely detailed medical records on employees. Larger companies may have an epidemiologist who studies the incidence of disease in their workers. Smaller companies may not have as detailed medical records on employees as larger companies, and they may not keep them over an extended period of time.

8.4 Molecular/Atomic Structural Analysis

Chemistry is the science of the combination of atoms, and physics is the science of the forces between atoms. Simply stated, chemistry deals with matter and its transformations, and physics deals with energy and its transformations. These transformations may be temporary, such as a change in phase, or seemingly permanent, such as a change in the form of matter resulting from a chemical reaction. The study of atomic and molecular structure deals with these transformations and can be used to make a preliminary identification of a health hazard.

Molecular structural analysis is a developing method. The objective of a molecular structural analysis is to demonstrate a physical, structural, or chemical similarity between the chemical in question and a known toxic chemical that produces toxic and health effects in experimental animals and/or humans (this is also called structure–activity relationships). Unfortunately, scientists do not fully understand the effects of slight changes in the chemical structure and their biological effects on humans. As a result, this type of analysis is useful only in preliminary studies to identify potential health hazards for further examination with more established methods in short-term tests or tests in experimental animals. In its present stage of development, molecular structural analysis cannot be used to make absolute decisions about the appropriate levels of exposure of humans to chemicals [3].

There are two logical approaches for applying atomic and molecular structural analysis for the purpose of identifying health hazards: the *synthetic* approach and the *analytical* approach. A synthetic approach begins with an analysis of the structure and behavior of matter in its simplest state. This approach then progresses to more complex states of matter, from electrons to atoms to molecules, then to combinations of atoms and molecules, then to combinations resulting from chemical reactions. The analytical approach begins with known matter or chemicals found in the laboratory and works toward simpler states of subdivision in order to explain experimental results.

Illustrative Example 8.7

What are the structural and molecular formulae for the following toxic air compounds?

1. Tetrachloroethene
2. 2,3,7,8-Tetrachlorodibenzodioxin (TCDD)

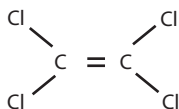
Solution

Molecular formulae

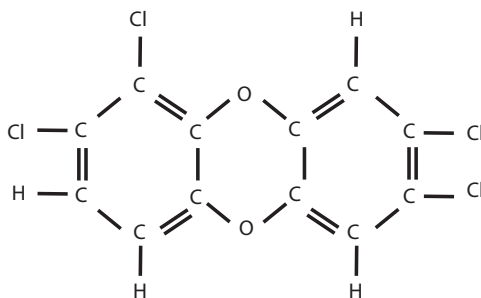
1. Tetrachloroethene: C_2Cl_4
2. 2,3,7,8-Tetrachlorodibenzodioxin: $C_{12}H_4O_2Cl_4$

Structural formulae

1. Tetrachloroethene



2. 2,3,7,8-Tetrachlorodibenzodioxin

**Illustrative Example 8.8**

With reference to priority water pollutants, provide the chemical formula for the following five pollutants:

1. Anthracene
2. Chrysene
3. Diethyl phthalate
4. Methylene chloride
5. Naphthalene

Solution

The chemical formula for each pollutant is provided in the following:

1. Anthracene: $C_{14}H_{10}$
2. Chrysene: $C_{18}H_{12}$
3. Diethyl phthalate: $C_{12}H_{14}O_4$
4. Methylene chloride: CH_2Cl_2
5. Naphthalene: $C_{10}H_8$

8.5 Material Safety Data Sheets

The MSDS has, over the past 35+ years, become the major media for transmitting health and hazard information concerning chemicals. MSDSs have also played a key role in health and hazard communication programs [5].

MSDS preparers and users have discovered that there are many aspects to their preparation that can affect their utility. Since MSDSs have multiple audiences, their preparation has become a complicated process. The preparation and use of MSDSs have thus become an evolving and ongoing process. On the global scene, there is increasing pressure to try to develop an international standard for MSDSs, so the same document can be used in different international markets.

The MSDS is a detailed information bulletin prepared by the manufacturer or importer of a chemical that describes its formulation, composition, precautions for proper use and handling, as well as the potential physical and health problems it might pose to users. The MSDS details routes of exposure, emergency and first aid procedures, and control measures in case of an uncontrolled release. Information on an MSDS aids in the selection of safe products and helps prepare employers and employees to respond effectively to daily exposure situations as well as to emergency releases. It is also a source of information for identifying chemical hazards (accidents), a topic treated in Part III.

In line with the Occupational Safety and Health Administration (OSHA) requirements, employers must maintain a complete and accurate MSDS for each hazardous chemical that is used in their facility. They are entitled to obtain this information automatically upon purchase of the material. When new and significant information becomes available concerning a product's hazards or ways to protect against the hazards, chemical manufacturers, importers, or distributors *must* add it to their MSDS within 3 months and provide this updated information to their customers with the next shipment of the chemical. If there are multiple suppliers of the same chemical, there is no need to retain multiple MSDSs for that chemical.

While MSDSs are not required to be physically attached to a shipment, they must accompany or precede the shipment. When the manufacturer/supplier fails to send an MSDS with a shipment labeled as hazardous, the employer must obtain one from the chemical manufacturer, importer, or distributor as soon as possible. Similarly, if the MSDS is incomplete or unclear, the employer should contact the manufacturer or importer to seek clarification or obtain missing information.

When an employer is unable to obtain an MSDS from a supplier or manufacturer, he or she should submit a written complaint, with complete background information, to the nearest OSHA area office. OSHA will then call and send a certified letter to the supplier or manufacturer to obtain the needed information. If the supplier or manufacturer still fails to respond within a reasonable time, OSHA will inspect the supplier or manufacturer and take appropriate enforcement action against them.

It is important to note that OSHA specifies the information to be included on an MSDS but does not prescribe the precise format for an MSDS. A non-mandatory MSDS form that meets the Hazard Communication Standard requirements can be used as is or expanded as needed. The MSDS must be in English and must include at least the information presented in Table 8.2. In

TABLE 8.2**MSDS Information**

Chemical identity	<ul style="list-style-type: none"> • The chemical and common names must be provided for single chemical substances. • An identity on the MSDS must be cross-referenced to the identity found on the label.
Hazardous ingredients	<ul style="list-style-type: none"> • For a hazardous chemical mixture that has been tested as a whole to determine its hazards, the chemical and common names of the ingredients that are associated with the hazards and the common name of the mixture must be listed. • If the chemical is a mixture that has not been tested as a whole, the chemical and common names of all ingredients determined to be health hazards and compromising 1% or greater of the composition must be listed. • Chemical and common names of carcinogens must be listed if they are present in the mixture at levels of 0.1% or greater. • All components of a mixture that have been determined to pose a physical hazard must be listed. • Chemical and common names of all ingredients determined to be health hazards and comprising less than 1% (0.1% for carcinogens) of the mixture must also be listed if they can still exceed an established OSHA Permissible Exposure Limit (PEL) or the ACGIH Threshold Limit Value (TLV) or present a health risk to exposed employees in these concentrations. Chapter 9 will address PELs and TLVs in further detail.
Physical and chemical characteristics	<ul style="list-style-type: none"> • The physical and chemical characteristics of the hazardous substance must be listed. These include items such as boiling and freezing points, density, vapor pressure, specific gravity, solubility, volatility, and the product's general appearance and odor. These characteristics provide important information for designing safe and healthy work practices.
Fire and explosion hazard data	<ul style="list-style-type: none"> • The compound's potential for fire and explosion must be described. Also, the fire hazards of the chemical and the conditions under which it could ignite or explode must be identified. Recommended extinguishing agents and firefighting methods must be described.
Reactivity data	<ul style="list-style-type: none"> • This section of the MSDS presents information about other chemicals and substances with which the chemical is incompatible or with which it reacts. Information on any hazardous decomposition products, such as carbon monoxide, must be included.
Health problems	<ul style="list-style-type: none"> • The acute and chronic health problem of the chemical, together with signs and symptoms of exposure, must be listed. In addition, any medical conditions that are aggravated by exposure to the compound must be included. The specific types of chemical health hazards defined in the standard include carcinogens, corrosives, toxins, irritants, sensitizers, mutagens, teratogens, and effect on target organs (i.e., liver, kidney, nervous system, blood, lungs, mucous membranes, reproductive system, skin, eyes, etc.) • The route of entry section describes the primary pathway by which the chemical enters the body. There are three principal routes of entry: inhalation, skin, and ingestion

TABLE 8.2 (continued)

MSDS Information

	<ul style="list-style-type: none"> • This section of the MSDS supplies the PEL, the TLV, and other exposure levels used or recommended by the chemical manufacture. • If OSHA, the National Toxicology Program (NTP), or the International Agency for Research on Cancer (IARC) list the compound as a carcinogen (cancer causing agent), it must be indicated as such on the MSDS.
Precautions for safe handling and use	<ul style="list-style-type: none"> • The standard requires the preparer to describe the precautions for safe handling and use. These include recommended industrial hygiene practices, precautions to be taken during repair and maintenance of equipment, and procedures for cleaning up spills and leaks. Some manufacturers also use this section to include useful information not specifically required by the standard, such as EPA waste disposal methods plus state and local requirements.
Control measures	<ul style="list-style-type: none"> • The standard requires the preparer of the MSDS to list any generally applicable control measures. These include engineering controls, safe handling procedures, and personal protective equipment. Information is often included on the use of goggles, gloves, body suits, respirators, and face shields.
Employer's responsibilities	<ul style="list-style-type: none"> • Employers must ensure that each employee has a basic knowledge of how to find information on an MSDS and how to properly make use of that information. Employers also must ensure the following: <ul style="list-style-type: none"> • Complete and accurate MSDSs are made available during each work shift to employees when they are in their work areas. • Information is provided for each hazardous chemical.

reviewing this material, the reader should understand the effect and importance of each subsection in helping to identify a chemical hazard, particularly the section on health hazards.

Illustrative Example 8.9

Qualitatively describe in "layman's language" the health and safety information that is provided on an MSDS.

Solution

An MSDS serves as a reference source for information on a hazardous substance. The MSDS identifies the substance, the producer or seller of the substance, and the location of the producer or seller; explains why the substance is hazardous and how a person can be exposed to the substance; identifies conditions that increase the hazard; explains safe handling procedures; identifies proper protective clothing or devices to be used when working with the substance; explains the steps that should be taken if a person is exposed to the substance; and explains the steps that should be taken if there is a spill or emergency situation.

Illustrative Example 8.10

Discuss some of the limitations of MSDS use.

Solution

The information contained in the MSDS is highly variable and is dependent on the supplier's knowledge and expertise. Work is in progress to improve the quality of information in MSDSs and (as noted earlier) to standardize the MSDS format. The American National Standards Institute (ANSI) has developed a MSDS format.

Understanding of terminology used in MSDSs can be a problem for some employees. Additional training and use of supplemental information can help in dealing with this problem.

Illustrative Example 8.11

Explain why first aid measures should be included in an MSDS.

Solution

First aid measures are included in an MSDS to provide the user with the information needed to assist someone who has been exposed to a chemical. The MSDS may suggest basic first aid measures that can be provided until professionals arrive or when professional assistance is not required. Depending on the chemical and the type of exposure, basic first aid measures may include moving the victim to fresh air or flushing the eyes with water.

Illustrative Example 8.12

Describe the physical and chemical characteristics included in an MSDS. Explain why this information should be included in an MSDS.

Solution

The physical and chemical characteristics that are included in an MSDS are the boiling point, melting point, vapor pressure, vapor density, evaporation rate, solubility in water, specific gravity, and a description of the normal appearance and odor of a chemical. The boiling and melting points are included in an MSDS to make the user aware that protective measures may need to be taken to prevent a potentially dangerous change in state. The vapor pressure, vapor density, and evaporation rate are included to make the user aware that protective measures may need to be taken against flammable or toxic gases and vapors. The solubility in water and specific gravity inform the user of the state of the chemical when added to water, i.e., whether the chemical may dissolve in water, sink, or float. A description of the normal appearance and odor of a chemical in an MSDS helps the user recognize a potentially dangerous situation.

Illustrative Example 8.13

Provide a one-sentence explanation of the need for each piece of information on a typical MSDS sheet. (The reader may choose to refer to Illustrative Example 6.14 for similar explanations.)

Solution

1. *Product or chemical identity used on the label:* This ensures that the correct chemical is being used and alerts the worker to the potential hazards of working with the chemical.
2. *Manufacturer's name and address:* Contacting the manufacturer would help clarify any uncertainties concerning the chemicals being used and could also, in the event that it has been discovered that the manufacturer has made an error in the production or delivery of a certain chemical, prevent a potential catastrophe elsewhere caused by the use of the same chemical.
3. *Chemical and common names of each hazardous ingredient:* This serves as a reference for those working with chemicals to check and see if the chemicals being used are hazardous.
4. *Name, address, and phone number for hazard and emergency information:* Their assistance may be necessary if an accident should occur or if there is any uncertainty concerning a certain chemical.
5. *Hazardous chemical's physical and chemical characteristics, such as vapor pressure and flashpoint:* This information can be used to control the environment that the hazardous chemical is going to be used in.
6. *Physical hazards, including potential for fire, explosion, and reactivity:* This aids in the analysis of a "worst-case" scenario that could result from a simple accident.
7. *Known health hazards:* This alerts workers to use special caution when working with the hazardous materials.
8. *Exposure limits:* This helps to protect those working with the material.
9. *Emergency and first aid procedures:* In the event of an accident, these procedures could save an afflicted worker's life.
10. *Toxicological information:* Alerts workers to the potential risk of developing cancer or other diseases from working with the substance and encourages special caution to be taken in working with the substance.
11. *Precautions for safe handling and use:* This helps to protect those working with the material.
12. *Control measures such as engineering controls, work practices, hygienic practices, or personal protective equipment required:* These measures are specified in an attempt to minimize the risk involved in working with hazardous materials.
13. *Procedures for spills, leaks, and cleanup:* These procedures are used to minimize the damage caused by the accidental release of the chemical.

Illustrative Example 8.14

Provide physical, chemical, and health-related data on 4,4-DDT. (Note: This and the next two illustrative examples refer to acronyms not previously described in this chapter. However, all the toxicology acronyms will be described in detail in Chapter 9.)

Solution

Adapted from A. Spero, B. Devito, and L. Theodore, *Regulatory Chemicals Handbook*, Marcel Dekker (acquired by CRC Press/Taylor & Francis Group, Boca Raton, FL), New York, 2000.

4,4-DDT ($C_{14}H_9Cl_5$, MW = 354.5)

CAS/DOT identification number: 50-29-3/UN 2761

Synonyms. *p-p'*-DDT, DDT, 2,2-bis(*p*-chlorophenyl)-1,1,1-trichloroethane, dichloro-diphenyltrichloroethane, dicophane, chlorophenothane, Gesarol®, Neocid®

Physical properties. waxy solid; weak, chemical odor; tasteless; sinks in water; MP (107°C–109°C); BP (185°C); SG (1.56 at 15°C); VP (1.9×10^{-7} torr at 20°C); solubility in water (0.006 mg/L at 25°C)

Chemical properties. Incompatible with strong oxidizers; may react with iron, aluminum, aluminum and iron salts, and alkalis; incompatible with ferric chloride and aluminum chloride; FP (72°C–75°C)

Biological properties. Long-term persistence in soil and water; sticks strongly to soil particles and does not leach rapidly into underground water; soil half-life: 2–15 years; aerobic half-life: 2–15.6 years; anaerobic half-life: 16–100 days; surface water half-life: 7–350 days; ground water half-life: 16–31.3 days; can be detected in water by EPA Method 608: gas chromatography or EPA Method 625: gas chromatography plus mass spectrometry

Bioaccumulation. Concentrated accumulation in the fat of wild-life and humans as a result of low water solubility and high lipophilicity; builds up in plants and in the fatty tissues of fish, birds, and animals

Origin/industry sources/uses. Manufactured chemical; used to control insects on agricultural crops and insects that carry diseases like malaria and typhus; ectoparasiticide; use was banned in United States in 1972

Toxicity. No data available

Exposure routes. Inhalation; skin adsorption; ingestion; eye and skin contact; eating contaminated foods such as root and leafy vegetables, meat, fish, and poultry; inhalation of contaminated air or drinking contaminated water near waste sites and landfills; swallowing soil particles near waste sites or landfills

Regulatory status. Criterion to protect freshwater aquatic life: 0.0010 µg/L/24h avg., concentration not to exceed 1.1 µg/L any time; criterion to protect saltwater aquatic life: 0.0010 µg/L/24h avg., concentration not to exceed 0.13 µg/L

any time; criterion to protect human health: preferably 0, concentration calculated to keep the lifetime cancer risk level below 10^{-5} is 0.24 ng/L; USSR MAC: 0.1 mg/L in water used for domestic purposes, 0 in surface water for fishing; Mexico MPC: 0.042 mg/L in drinking water, 0.006 mg/L in estuaries, and 0.6 $\mu\text{g/L}$ in coastal waters; the following are guidelines in drinking water set by some states: 0.83 $\mu\text{g/L}$ (Maine), 0.42 $\mu\text{g/L}$ (Kansas), 1.0 $\mu\text{g/L}$ (Minnesota), and 50 $\mu\text{g/L}$ (Illinois)

Probable fate. Photolysis: photooxidation to DDE occurs slowly; indirect photolysis may be important; oxidation: photooxidation occurs, photooxidation half-life in water: 7–350 days, photooxidation half-life in air: 7.4 days; hydrolysis: it may be an important process under certain conditions, first-order hydrolytic half-life: 22 years; volatilization: it is an important process, some will evaporate from soil and surface water into the air; sorption: it is an important process, will adsorb very strongly to soil if released to the soil, and will adsorb very strongly to sediments if released to water; biological processes: biotransformation and bioaccumulation are important processes, may be subject to biodegradation in flooded soils or under anaerobic conditions, may be significant in sediments

Treatability/removability (process, removal [%], avg. achievable conc. [$\mu\text{g/L}$]). Sedimentation with chemical addition (alum, lime): >52, <1; activated sludge (based on synthetic wastewater): 0, not available; powdered activated carbon adsorption (based on synthetic wastewater): ~100, 0.008; continuous activated sludge biological treatment simulator: removal was 100%, 0; wet and dry deposition: it will be major removal mechanisms from the air

In addition to Spero et al. referenced earlier, the reader may refer to the following references for additional details on this chemical:

1. R. Lewis, *Sax's Dangerous Properties of Industrial Materials*, 9th edn., Van Nostrand Reinhold, New York, 1996.
2. *Suspect Chemicals Sourcebook*, Roytech Publications, Bethesda, MD, 1996.

Illustrative Example 8.15

An OSHA chemical of major concern to the government, industry, and public is mercury. Provide key information on this chemical.

Solution

Mercury, aryl and inorganic compounds (Hg, MW = 200.6)

CAS/DOT identification number: 7439-97-6/UN2809

Synonyms. Synonyms may vary depending upon specific compound

Physical properties. Most inorganic mercury compounds are white powders or crystals; mercuric sulfide (cinnabar) is red and

turns black when exposed to light; insoluble in hydrochloric or similar acids; soluble in nitric acid and hot concentrated sulfuric acid; water soluble salts include mercuric chlorate, cyanide, chloride, and acetate; oxides, sulfates, and most other common salts, including mercurous chloride, are sparingly soluble or decomposed in water; appearances vary from colorless crystals to yellow, red (oxide, sulfide, iodide), and brown or black (sulfide); MP (-39°C , -38°F); BP (357°C , 674°F); DN (13.534 g/cm^3 at 25°C); SG (13.5); VD (not applicable); VP (0.0012 mmHg at 20°C)

Chemical properties. Mercury salts yield metallic mercury when heated with sodium carbonate; mercury salts may be reduced to metal by hydrogen peroxide in the presence of alkali hydroxide; soluble ionized mercuric salts give a yellow precipitate or mercuric oxide with sodium hydroxide and a red precipitate of mercury diiodide with alkali iodide; mercurous salts give a black precipitate with alkali hydroxides and a white precipitate of mercurous chloride (calomel) with hydrogen chloride or soluble chlorides; decomposes slowly on exposure to sunlight

Explosion and fire concerns. Not combustible; NFPA rating (not rated); mercurous chloride is incompatible with bromides, iodides, alkali chlorides, sulfates, sulfites, carbonates, hydroxides, ammonia, silver salts, copper salts, hydrogen peroxide, iodine, and iodoform; mercuric oxide reacts explosively with acetyl nitrate, chlorine and hydrocarbons, butadiene and ethanol and iodine (at 35°C), and hydrogen peroxide and traces of nitric acid; forms heat- or shock-sensitive explosive mixtures with metals and nonmetals; contact with acetylene, acetylene products, or ammonia gases may form solid products that are sensitive to shock and which can initiate fires of combustible materials; decomposition emits highly toxic fumes of Hg; use water spray, fog, or foam for firefighting purposes

Health symptoms. Inhalation (irritates eyes, skin, and respiratory system); skin absorption (central nervous system damage, kidney damage, and weight loss)

First aid. Wash eyes immediately with large amounts of water; wash skin immediately with soap and water; provide oxygen and respiratory support

Human toxicity data. Inhalation-man TDLo, $44,300\mu\text{g/m}^3/8\text{ h}$; toxic effect: central nervous system, liver, MET; inhalation-woman TDLo, $150\mu\text{g/m}^3/46\text{ days}$; toxic effect: central nervous system, gastrointestinal tract; skin-man TDLo, $129\text{ mg/kg}/5\text{ h}$; toxic effect-ear, central nervous system, skin

Acute health risks. Irritation of eyes, skin, and mucous membranes; severe nausea; vomiting; abdominal pain; renal damage; prostration; chest pain; dyspnea; bronchitis; pneumonitis; insomnia; headache; fatigue; weakness; irritability; gastrointestinal disturbances; anorexia; low weight; proteinuria

Chronic health risks. Tremors; trouble remembering and concentrating; increased salivation; gum problems; loss of appetite and weight; changes in mood and personality; hallucinations;

psychosis; clouding of the eyes; skin allergies; grayish skin color; kidney damage; decreased sex drive

Exposure guidelines. ACGIH TLV TWA, 0.1 $\mu\text{g}(\text{Hg})/\text{m}^3$ (skin); OSHA PEL CL, 0.1 mg (Hg)/ m^3 (skin); NIOSH REL CL, 0.1 mg/ m^3 (skin); IDLH, 10 mg (Hg)/ m^3

Personal protection. Wear full protective clothing (suits, gloves, footwear, headgear, etc.); wear chemical safety goggles and face shield; full facepiece respiratory protection is recommended; eye wash fountains should be provided in the immediate work area

Spill cleanup. Ventilate area of spill; use a specialized charcoal-filtered vacuum or suction pump to collect all visible material; sprinkle the entire area of the spill with elemental zinc powder; use a 5%–10% sulfuric acid solution to dampen the zinc powder to create a paste-like consistency; after paste dries to a light gray color, it may be swept up and disposed of properly; residual material is removed with soap and water

Disposal and storage methods. Contain and dispose of mercury as a hazardous waste; contact the Department of Environmental Protection (or the equivalent) or the regional office of EPA for specific recommendations; store in tightly closed containers in a cool, well-ventilated area; keep away from acetylene, ammonia, and nickel; store in secure poison area

Regulatory information. AI; DOT hazard class/division (6.1); labels (poison)

Other comments. Inorganic salts of mercury, such as ammoniated mercuric chloride or mercuric iodide, have been used in skin lightening creams; mercuric chloride has been used as a topical antiseptic or disinfectant agent; mercuric sulfide and mercuric oxide are used as pigments in paints; mercuric sulfide is also used as a pigment for tattoos; some inorganic mercury compounds are also used in fungicides

Illustrative Example 8.16

Provide key information on the toxic chemical 2,3,7,8-tetrachloro dibenzo-*p*-dioxin.

Solution

The following information was adapted from J. Spero, B. Devito, and L. Theodore, *Regulatory Chemicals Handbook*, Marcel Dekker (acquired by CRC Press, Taylor & Francis Group, Boca Raton, FL), New York, 2000.

2,3,7,8-Tetrachlorodibenzo-*p*-dioxin ($\text{C}_{12}\text{H}_4\text{Cl}_4\text{O}_2$, MW = 321.96)

CAS/DOT identification number: 1746-01-6

Synonyms. Dioxin, dioxine, TCBDB, TCDD, 2,3,7,8-TCDD, tetradioxin

Physical properties. White, crystalline solid or colorless needles; slightly soluble in water; BP (412.2°C, 774°F); MP (305°C, 581°F); DN (1.827 g/mL at 20°C); VP (1.52E-09 mmHg at 25°C)

Chemical properties. Caustic

Exposure routes. Inhalation (fly ash, soot particles, flue gases, ambient air, incineration fumes, herbicides, and wood dust), ingestion (urban vegetation, fish, and cow's milk), occupational exposure in pulp and paper, wood industries

Human health risks. Probable human carcinogen; acute risks: irritation of skin and eyes; tightness in chest; dizziness; headache; nausea; allergic dermatitis; hepatic necrosis; thymic atrophy; hemorrhage; chloracne; chronic risks: skin lesions; chloracne; severe weight loss; pancreatic, bronchogenic carcinoma; gastric ulcers; delayed death

Hazard risk. Most toxic member of the dioxin family; caustic and corrosive

Measurement methods. Not available

Major uses. By-product of herbicides, defoliants, and Agent Orange; research chemicals; wood preservative (not commercially)

Storage. Not available

Firefighting. Not available

Personal protection. Wear gastight and Viton⁷ rubber gloves; wear approved chemical safety goggles; material should be handled or transferred in an approved fume hood or with adequate ventilation; electrically ground all equipment when handling this product; a NIOSH-approved air-supplied respirator is recommended in absence of proper environmental controls; maintain eyewash baths and safety showers in work area

Spill cleanup. Consider evacuation; contain release and eliminate its source, if this can be done without risk, remove any sources of ignition until the area is determined to be free from explosion or fire hazards

Health symptoms. Inhalation (headache, dizziness, hallucinations, changes in motor activity, nausea, respiratory irritation); skin (prickling, allergic dermatitis); eyes (severe irritation); ingestion (dizziness, headache, nausea, drowsiness, tightness of chest)

General comments. Oral rat LD₅₀ 20 g/kg; first aid: immediately wash eyes with large amounts of water; if skin contact occurs, remove clothing and flush skin with large amounts of water and soap; if inhaled, move to fresh air and provide respiratory assistance as needed

In addition to Spero et al. listed earlier, the reader may refer to following references for specific details on this chemical:

1. R. Lewis, *Sux's Dangerous Properties of Industrial Materials*, 9th edn., Van Nostrand Reinhold, New York, 1996.
2. *Suspect Chemicals Sourcebook*, Roytech Publications, Bethesda, MD, 1996.

Illustrative Example 8.17

What is the difference between hazardous chemicals and toxic chemicals?

Solution

Hazardous chemical is a broad category that includes chemicals that may be toxic, flammable, corrosive, explosive, or harmful to the environment. A toxic chemical is one type of a hazardous chemical. Toxic chemicals cause adverse health effects (such as cancer, other severe illness, or death) when ingested, inhaled, or absorbed by a living organism.

Illustrative Example 8.18

Describe the dioxin/furan family of chemicals.

Solution

Dioxin is a term used to describe a large group of chemical compounds having a similar basic structure. The most common subgroup of dioxin compounds (of which there are 75 different varieties) comprises those that include chlorine atoms. A few are toxic; the most toxic is 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (2,3,7,8-TCDD); see Illustrative Example 8.16. There are also 135 polychlorinated-dibenzofuran compounds. These are known as “furans.”

These compounds are chlorinated tricyclic aromatic compounds. Each of these compounds has a triple-ring structure consisting of two benzene rings interconnected to each other by, respectively, one or two oxygen atoms. The number of chlorine atoms can vary between one and eight. The PCDD (dioxin) and PCDF (furan) compounds are referred to as “congeners”—a specific member of a group of structurally related compounds. The most widely discussed chemical, 2,3,7,8-TCDD, is a colorless crystalline solid, is slightly soluble in water, and binds strongly to solids and particulate matter.

The known natural sources of PCDDs and PCDFs are related to fires and combustion processes. Thus, these toxic compounds may be produced from forest fires, by lightning or volcanic action. The formation of PCDDs/PCDFs is very dependent on the presence of oxygen, carbon, chlorine, and heat. Since fire produces PCDDs/PCDFs, combustion devices may have emissions of these compounds. These include municipal waste incinerators, industrial waste incinerators, medical waste combustors, sewage sludge incinerators, wood and coal combustion, and oil combustion including motor vehicle engines and accidental fires.

Additional details on 2,3,7,8-TCDD were provided earlier in this chapter.

Illustrative Example 8.19

Which one of the following statements is true of the organic pollutants 2,3,7,8-tetrachloro-*p*-dioxin and 2,3,7,8-tetrachlorodibenzofuran?

1. They are formed in post-furnace reactions in cyclones and electrostatic precipitators.
2. They are found inside municipal solid waste incinerator facilities at higher levels in summer than in winter.

3. The average ambient air outside the municipal solid waste incinerator facility contains the same amount of these pollutants as the human work area inside the facility.
4. The mechanism of their formation is known.

Solution

1. *True.* Combustion units are a primary source of dioxins and furans in the workplace. They are probably emitted from the back pressure or leakage from boilers.
2. *False.* There is more ventilation in municipal solid waste incinerators during the summer because of open windows and air conditioners; thus, there is a lower level (lower concentration) of pollution indoors in the summer than in the winter.
3. *False.* The concentration of dioxins and furans inside a solid waste incinerator facility was significantly higher than was found in the ambient air sampled in several locations throughout Ohio (where a study was conducted nearly 20 years ago).
4. *False.* The exact mechanism of formation was not known at the time of the preparation of this chapter.

Therefore, the correct answer is 1.

8.6 Engineering Problem Solving

Perhaps the most important job that the practicing engineer faces on a day-to-day basis is the need to solve problems. Several problem-solving approaches are presented in Part III in an attempt to identify hazards (particularly of an accidental nature). These problem-solving methods include, but are not limited to:

1. "What if" approaches
2. Hazard and operability (HAZOP) studies
3. Preliminary hazard analysis (PLHA)
4. Process hazard analysis (PHA)
5. Safety reviews
6. Safety audits

These problem-solving methods often involve a need to determine the following:

- What is known
- What is unknown
- What is desired or required

Additionally, questions often arise regarding the identity, location, timing, and magnitude of the problem.

Although the aforementioned approaches cannot always be directly applied to identifying health problems, the general methodology is applicable to identifying health concerns since these are basic problem-solving approaches [6]. The following procedure is a sample problem-solving approach for engineers and scientists [7]. For the purposes of this section, this procedure is presented as a problem-solving approach for chemical health problem identification; however, this procedure can also be used to solve a near-infinite number of engineering problems, including hazard identification problems.

1. Identify the problem. Understand the information available and the requirements for the answer.
2. Determine what additional information is required and obtain it.
3. If applicable, draw a simplified picture or diagram of what is taking place and include the available data.
4. Determine a basis on which to start the problem.
5. If chemical equations are involved, write those equations and verify that they are balanced.
6. Decide which formulas or relations govern the particular health hazard.
7. If applicable, perform the necessary calculations.
8. Determine whether the conclusion regarding the status of the health hazard seems reasonable.

8.7 Fate of Chemicals in the Environment Related to Health Problems

In the process of identifying chemical health problems, the near-term and long-term fate of the chemical should be incorporated into the analysis. Near-term concerns relate primarily to the release of the chemical into the environment. This leads to the general subject area of exposure assessment, including routes of exposure, a topic that is treated in extensive detail in Chapter 10. However, the fate of a chemical following the point of entry into the human body is another consideration when attempting to identify health problems. An overview of this topic is presented here [2].

As one might expect, exposure to a chemical results in a response by the human body. The body responds to a chemical with physiological (metabolic) processes in order to absorb, distribute, store, transform, or eliminate

that chemical. To become a chemical health problem, the chemical, or the transformation product of that chemical, must reach a target organ for a sufficient length of time and at a sufficient concentration to produce toxic effects. A target organ is the "preferential anatomical site" for the expression of toxic effects by a chemical substance in the human body.

Consider the routes of exposure of the chemical benzene and the physiological response by the human body to that chemical. The route of exposure of a dose of benzene vapors into the body is inhalation. The body will absorb 30% of the inhaled dose into the lungs and blood. The body will eliminate the remaining 70% of the inhaled amount by exhalation. Another route of exposure exhibited in laboratory animals is ingestion. The body will absorb more than 90% of an ingested dose of benzene. The least effective route of exposure is dermal exposure, with only approximately 0.2% of the dose absorbed transdermally into the body. In the body, more than half of the benzene that has been absorbed is distributed to organs with a rich blood supply, such as the liver and kidneys, and to tissues with a rich fat supply, such as adipose tissue, the brain, and bone marrow. In pregnant women, benzene is distributed to the placenta and fetus. Fatty tissues slowly release benzene, and the body transforms the nonpolar, fat-soluble benzene into polar metabolites that are eliminated in the urine by excretion. Although a substantial database exists for several chemical compounds such as benzene, the knowledge base for most substances is incomplete.

Most chemicals distribute throughout the body via the blood stream. In fact, few agents attack locally at entry; rather, most agents use the flow of blood to reach other organs and tissues. Distribution is affected by absorption, perfusion, exposure route, and tissue affinity. As a result, a chemical distributes itself throughout the body in different locations in different amounts rather than at the total dose in one location. Absorption determines the passage of the chemical into the blood and from the blood into tissues and cells. Perfusion is the movement of blood through organ tissue. Both the liver and brain are well perfused. The brain is protected by a barrier between the blood and the brain. On the other hand, the liver is not protected, and its total potential absorption of a chemical is much greater than that of the brain.

The exposure route partly determines the distribution of the chemical in the body. Like the chemical benzene, a single chemical may follow multiple routes of exposure. The liver, like the skin, acts as a filter. The liver is the primary detoxification site in the human body. Toxicants that are absorbed into the lungs, skin, mouth, and esophagus may temporarily bypass the liver; however, toxicants absorbed through the stomach and intestines follow the blood's direct path to the liver.

The term *storage* is used to describe a site or an organ that is not a target organ, but that exhibits a concentration of a chemical substance. Tissue affinity allows chemicals to be stored in tissues at these sites. The concentration at a storage site is sometimes as high as or higher than the concentration of

the chemical in the target organ. The storage site concentration and location depends on the chemical.

Storage may be a defense mechanism of the body. Chemicals are slowly released from the storage site. Through storage, the body temporarily eliminates the chemical substance, thus preventing or reducing a distribution of the chemical that may cause toxic effects in some target organ of the body. Storage acts in equilibrium with other systems in the body. This equilibrium can be reversed, thus allowing elimination of the stored chemical over time, even after the exposure has ended.

The site of accumulation may define the point of toxic action. Inorganic mercury accumulation in the kidneys causes severe functional impairment [8]. Kidney damage has been shown to occur when the total accumulation of cadmium in the kidney cortex reaches 100–200 ppm [9].

Biotransformation, elimination, and formation of a chemical–receptor complex are alternatives to storage. Biotransformation is the metabolism of the toxicant by enzyme-rich organs. The toxicant transforms into other molecular species known as metabolites, which may or may not be less toxic than the parent toxicant. Toxicants and metabolites that are not stored are eliminated by the body. These substances, particularly polar compounds, are eliminated through urine, bile, feces, or secretions. Nonpolar and nonvolatile compounds are more difficult for the body to eliminate. These substances can often be eliminated by urine after the toxic agent has been metabolically transformed into a more polar, and thus more water soluble, substance. Toxic agents attack one or more organs, known as target organs, by forming a chemical–receptor complex.

These mechanisms can affect the near-term as well as the ultimate severity of a chemical exposure. Recognition of these mechanisms can significantly assist in the identification of a chemical agent as a health problem. In recent years, the understanding of chemical transport, chemical manipulation in the body, and response by animals and humans to chemicals has advanced to a point where it is possible to determine whether exposure to a chemical will indeed result in a health problem.

Paustenbach [1] has provided an excellent review of the physical and chemical properties of substances and how this information is used to predict the fate of the substance in the environment and the human body. Although the details are beyond the scope of this section, the key factors affecting the fate of chemical substances are listed in the following:

1. Water solubility
2. Photodegradation (direct and indirect)
3. Biodegradation in soil
4. Vapor pressure and density
5. Dissociation content

6. Ultraviolet–visible (UV–Vis) absorption
7. Sorption and desorption
8. Partition coefficient
9. Bioconcentration factor (BCF)
10. Hydrolysis
11. Effects in algal assays
12. Effects on cellulose decomposition
13. Effects on nitrogen transformation
14. Effects on seed germination
15. Effects on sulfur transformation
16. Microbial growth inhibition

8.8 Carcinogens versus Noncarcinogens

The classification as to whether a chemical agent is a carcinogen or a non-carcinogen can help identify whether it is a health hazard. Both topics are briefly reviewed in this section [2]. More extensive information on this topic is provided in Chapter 9.

8.8.1 Noncarcinogens

Toxicity, i.e., the degree to which a chemical is considered a health problem, is characterized by its threshold. A threshold or lower limit below which effects cannot be observed characterizes the dose–effect or dose–response relationship. These effects can occur at the cellular, subcellular, and/or molecular level. The body protects itself against toxic chemicals with repair mechanisms and by attributing critical functions to large numbers of the same units. Thus, in order for a toxic effect to occur, a number of these units greater than the threshold for the target dose must be affected. For example, carbon tetrachloride is a solvent that causes disease in liver tissue. The body’s repair mechanism allows it to replace lost cells with new cells, thus allowing the liver to continue to function. Beyond a certain threshold, however, the liver cannot function and the damage cannot be reversed.

Noncarcinogenic effects include all toxicological responses except tumors. Toxicological responses and mechanisms vary widely, and examples of these include interference with normal cell processes by displacing elements out of the cell and binding with a cell to reduce membrane permeability. However, the majority of noncarcinogenic effects involve enzymes. In the body, different enzymes perform specific functions. When an enzyme binds with a

toxic substance, the enzyme may be prohibited from performing its function properly, thereby exhibiting a toxic response.

8.8.2 Carcinogens

Carcinogens cause cancer. Cancerous cells are normal cells that become abnormally altered and divide uncontrollably. The disease of cancer is characterized by tumors or neoplasms (meaning “new growth”); however, not all tumors are cancerous. Benign tumors are not cancerous and do not spread. Malignant tumors are cancerous and spread, or metastasize, to surrounding “structures.” This invasion of surrounding structures by malignant tumors occurs because the abnormal alteration of the cells prevents them from responding to the body’s regulatory signals that control cell growth.

As previously noted, carcinogenesis is the process that occurs between exposure to a carcinogenic chemical and the development of malignancy. The three stages of carcinogenesis are *initiation*, *promotion*, and *progression*. Initiation is the alteration or mutation of a normal cell into an abnormal cancerous cell. Promotion is the increase in the replication rate and number of initiated cells. Promotion is caused by promoting carcinogens. The promoter is not usually the same carcinogen that initiated the first stage of carcinogenesis. All cells that have been initiated and promoted do not develop into malignant cells. The body’s defense mechanism against foreign substances—the immune system—recognizes and rejects some of these cells. In progression, the third stage of carcinogenesis, the abnormal cells invade surrounding tissues and spread to distant organ sites. Progression involves more genetic mutations than those required in initiation and promotion.

References

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9

Toxicity and Dose–Response

9.1 Introduction

Dose–response assessment is the process of characterizing the relationship between the dose of an agent administered or received and the incidence of an adverse health effect in exposed populations. This process considers such important factors as intensity of exposure, age pattern of exposure, and other variables that might modify the response, such as sex and lifestyle. In effect, it involves the evaluation of the effects expected from various levels of a particular chemical in the environment. Dose and response are therefore fundamental concepts that provide a relationship between the dosage of a toxic agent and the biological response. The magnitude of the biological response depends on the concentration of the contaminant/physical agent at the site of action, while the concentration of the contaminant at the active site depends on the dose. Thus, the dose and the response are causally related. Toxicity data exhibit a dose–response *relationship* if a mathematical model can be formulated to describe the response of the receptor and/or test organism in terms of the dose administered. The relation often takes the form of a percentage or number of receptors responding in a given manner either to a dose or to a specified range of concentrations over a given period of time. A dose–response assessment usually requires extrapolation from high to low doses and extrapolation from animal to humans or one laboratory animal species to a wildlife species. A dose–response assessment should also describe and justify the methods of extrapolation used to predict incidence, and it should characterize the statistical and biological uncertainties in these methods. When possible, the uncertainties should be described numerically rather than qualitatively (see Section 9.7).

Why is toxicology important? As noted earlier, it is the dose that makes the poison. A low-level dose may cause no effect. Yet, a larger dose may lead to either an adverse health effect or even death. This dose variation is also a function of the chemical of concern. Furthermore, the manner in which the dose impacts a chemical's absorption, distribution, metabolism, and ultimate excretion from the human body can vary with both the chemical and the dose.

Once again, it is important to differentiate between the term *chronic* and *acute* as they relate to toxicity. *Chronic toxicity* is caused by long-term or repeated exposures to low doses and the intensity is usually less than with acute exposures. *Acute toxicity* is caused by large doses of a chemical over short time periods, as when the time between the exposure and the onset of a health problem is short. The intensity of acute toxicity effects is usually greater than from chronic toxicity exposure, and the receptor(s) usually have little opportunity to detoxify, eliminate, or adapt to the administered dose of an acutely toxic agent.

This chapter focuses on the general subject of toxicology and its companion topic, dose–response. The following section headings and subject areas are addressed following this introductory section:

Definitions

Toxicology

Epidemiology

Noncarcinogens

Carcinogens

Uncertainties/limitations

9.2 Definitions

Before proceeding to some of the more technical aspects of toxicology and the general subject of dose–response, several important definitions used by the profession and appearing in the literature are provided below (in alphabetical order).

Acceptable daily intake (ADI). An estimate similar in concept to the reference dose (RfD) but derived using a less strictly defined methodology. RfDs have replaced ADIs as the EPA's preferred values for use in evaluating potential noncarcinogenic health effects resulting from exposure to a chemical.

Acceptable intake for chronic exposure (AIC). An estimate similar in concept to the RfD but derived using a less strictly defined methodology. Chronic RfDs have replaced AICs as the EPA's preferred values for use in evaluating potential noncarcinogenic health effects resulting from chronic exposure to a chemical.

Acceptable intake for subchronic exposure (AIS). An estimate similar in concept to the subchronic RfD but derived using a less strictly defined methodology. Subchronic RfDs have replaced AISs as the EPA's preferred values for use in evaluating potential noncarcinogenic health effects resulting from subchronic exposure to a chemical.

Acute toxicity. The adverse effect occurring within a short time of (oral) administration of a single dose of a substance or multiple doses given within 24 h.

Carcinogen potency factor (CPF). A CPF is the slope of the dose–response curve at very low exposures. The units of a CPF are expressed as the inverse of daily dose (mg/kg-day^{-1}). See also *slope factor*.

Ceiling-recommended exposure limit (CREL). Exposure limit that should not be exceeded at any time.

Ceiling value (CV). The airborne concentration of a potentially toxic substance that should never be exceeded in the breathing zone.

Chronic reference dose (chronic RfD). An estimate (with an uncertainty spanning perhaps an order of magnitude or greater) of a daily exposure level for the human population, including sensitive subpopulations, that is likely to be without an appreciable risk of deleterious effects during a lifetime. Chronic RfDs are specifically developed to be protective for long-term exposure to a compound (the Superfund program guideline is 7 years to a lifetime).

Developmental reference dose (RfDdt). An estimate (with an uncertainty spanning perhaps an order of magnitude or greater) of an exposure level for the human population, including sensitive subpopulations, that is likely to be without an appreciable risk of developmental effects. Developmental RfDs are used to evaluate the effects of a single exposure event.

Dose. The amount of a substance available for interaction with metabolic processes or biologically significant receptors after crossing the outer boundary of an organism. The *potential* dose is the amount ingested, inhaled, or applied to the skin. The *applied* dose is the amount of a substance presented to an absorption barrier and available for absorption (although not necessarily having yet crossed the outer boundary of the organism). The *absorbed* dose is the amount crossing a specific absorption barrier (e.g., the exchange boundaries of skin, lung, and digestive tract) through uptake processes. *Internal dose* is a more general term denoting the amount absorbed without respect to specific absorption barriers or exchange boundaries. The amount of the chemical available for interaction by any particular organ or cell is termed the *deliverable dose* for that organ or cell.

Dose rate. This represents the dose per unit time, for example, in mg/day , also referred to as dosage. Dose rates are often expressed on a per-unit body-weight basis, yielding units such as mg/kg-day . They are often expressed as averages over some time period, e.g., a lifetime.

Dose–response curve. A graphical representation of the quantitative relationship between the administered, applied, or internal dose of a chemical or agent and a specific biological response to that chemical or agent.

Dose–response assessment. The process of quantitatively characterizing toxicity information and characterizing the relationship between the dose of a contaminant administered or received and the incidence of adverse health effects in the exposed population. Toxicity values can be derived from a quantitative dose–response relationship and used in the risk

characterization step to estimate the likelihood of adverse effects occurring in humans at different exposure levels. The assessment should attempt to take into account sex, lifestyle, and other modifying factors (MFs), as well as the extent of low-dose extrapolation. Whenever possible, the uncertainties should be expressed quantitatively rather than qualitatively.

EEGL. The concentration of a gas, vapor, or aerosol that is judged to be acceptable and that will allow exposed individuals to perform specific tasks during emergency conditions lasting from 1 to 24 h.

ERPG-1. The maximum airborne concentration below which an individual could be exposed for up to 1 h without experiencing an adverse health effect.

ERPG-2. The maximum airborne concentration below which an individual could be exposed for up to 1 h without experiencing or developing irreversible or other serious health effects.

ERPG-3. The maximum airborne concentration below which an individual could be exposed for up to 1 h without experiencing or developing life-threatening health effects.

Inhalation reference concentration (RfC). An estimate (with an uncertainty spanning perhaps an order of magnitude) of the daily exposure of the human population to a chemical, through inhalation, that is likely to be without risk of deleterious effects during a lifetime.

Integrated Risk Information System (IRIS). An EPA database containing verified RfDs and slope factors and up-to-date health risk and EPA regulatory information for numerous chemicals. IRIS is the EPA's preferred source for toxicity information for Superfund studies/projects.

Immediately dangerous to life and health (IDLH). The concentration representing the maximum level of a pollutant from which an individual could escape within 30 min without impairing symptoms or irreversible health effects.

LC_n. The concentration of a toxicant resulting from a single or limited exposure that is lethal to *n*% of a test population.

LD_n. The dose of a toxicant resulting from a single or limited exposure that is lethal to *n*% of a test population.

Lethal concentration 50 (LC₅₀). A calculated concentration of a chemical in air to which exposure for a specific length of time is expected to cause death in 50% of a defined experimental animal population. It is also referred to as the *median lethal concentration*.

Lethal dose 50 (LD₅₀). A calculated dose of a chemical in water to which exposure for a specific length of time is expected to cause death in 50% of a defined experimental animal population. It is also referred to as the *median lethal dose*.

Limit of detection (LOD). The minimum concentration of a substance being measured that, in a given matrix and with a specific method, has a 99% probability of being identified, qualitatively or quantitatively measured, and reported to be greater than zero.

Lowest observed adverse effect level (LOAEL). In dose-response experiments, the lowest exposure level at which there are statistically biologically

significant increases in frequency or severity of adverse effects between the exposed population and its appropriate control group.

Lowest observed effect level (LOEL). In dose–response experiments, the lowest exposure level at which there are statistically biologically significant increases in the frequency or severity of any effect between the exposed population and its appropriate control group.

Maximally exposed individual (MEI). The single individual with the highest exposure in a given population (also, maximum exposed individual). This term has historically been defined in various ways, including as defined here, and is also synonymous with worst case or bounding estimate.

Median effective concentration (EC). The concentration of toxicant or intensity of other stimulus that produces some selected response in 50% of a test population.

Median effective dose (ED). The statistically derived single dose of a substance that can be expected to cause a defined nonlethal effect in 50% of a given population of organisms under a defined set of experimental conditions.

Median lethal concentration (LC₅₀). The concentration of a toxicant that is lethal to one-half of a test population. It is also referred to as the *lethal concentration 50*.

Median lethal dose (LD₅₀). The statistically derived single dose of a chemical that can be expected to cause death in 50% of a given population of organisms under a defined set of experimental conditions. This value has often been used to classify and compare toxicity among chemicals but its value for this purpose is doubtful. One commonly used classification of this kind is provided in Table 9.1. It is also referred to as the *lethal dose 50*.

Method detection limit (MDL). See LOD.

NIOSH ceiling limit (NIOSH CL). NIOSH-recommended 15 min exposure limit, which should not be exceeded.

No observed adverse effect level (NOAEL). In dose–response experiments, an exposure level at which there are no statistically biologically significant increases in the frequency or severity of adverse effects between the exposed population and its appropriate control; some effects may be produced at this level, but they are not considered to be adverse, nor precursors to specific adverse effects. In an experiment with more than one NOAEL, the regulatory focus is primarily on the highest one, leading to the common usage of the term NOAEL to mean the highest exposure level without adverse effect.

TABLE 9.1

Lethal Dose 50 (LD₅₀) Classification

Category	LD ₅₀ Orally to Rat, mg/kg Body Weight
Very toxic	<25
Toxic	>25 to 200
Harmful	>200 to 2000

No observed effect level (NOEL). In dose–response experiments, an exposure level at which there are no statistically biologically significant increases in the frequency or severity of any effect between the exposed population and its appropriate control group.

Oral reference dose (ORfD). An estimate (with an uncertainty spanning perhaps an order of magnitude) of the daily exposure of the human population to a chemical, through ingestion, that is likely to be without risk of deleterious effects during a lifetime.

Permissible exposure limit (PEL). Expressed as a time-weighted average (TWA), the PEL is the concentration of a substance to which most workers can be exposed without adverse effects, averaged over a normal 8 h workday or a 40 h workweek.

Recommended exposure limit (REL). NIOSH-recommended exposure limit for an 8 or 10 h TWA exposure and/or ceiling.

Reference dose (RfD). The EPA's preferred toxicity value for evaluating non-carcinogenic effects resulting from exposures at Superfund sites.

Representativeness. The degree to which a sample is, or samples are, characteristic of the whole medium, exposure, or dose for which the samples are being used to make inferences.

Short-term exposure limit (STEL). The TWA airborne concentration to which workers may be exposed for periods up to 15 min, with no more than four such excursions per day and at least 60 min between them.

Slope factor. The slope factor is used to estimate an upper-bound lifetime probability of an individual developing cancer as a result of exposure to a particular level of a potential carcinogen. Also see *CPF*.

Subchronic permissible exposure guide line (SPEGL). The acceptable concentration for exposure of members of the general public. Subchronic generally refers to studies designed to examine the effects associated from repeated exposure over the life span of a test animal.

Suggested no adverse response level (SNARL). The maximum dose or concentration that, on the basis of current knowledge, is likely to be tolerated by an organism without producing any adverse effect.

Threshold limit value (TLV). The airborne concentration of a potentially toxic substance to which it is believed healthy working adults may be exposed safely through a 40 h working week and a full working life. This concentration is measured as a TWA concentration.

Threshold limit value ceiling (TLV-C). The concentration that should not be exceeded during any part of the working exposure. If conventional industrial hygiene instantaneous monitoring is not feasible, then the TLV-C can be assessed by sampling over a 15 min period, except for those substances that may cause immediate irritation when exposures are short.

Threshold limit value–short-term exposure limit (TLV-STEL). The concentration to which workers can be exposed continuously for a short period of time without suffering from irritation, chronic or irreversible tissue damage, or narcosis to a sufficient degree that may increase the likelihood of accidental

injury, impair self-rescue, or materially reduce work efficiency, and provided that the daily TLV-TWA is not exceeded. It is not a separate independent exposure limit; rather, it supplements the TWA limit where there are recognized acute effects from a substance whose toxic effects are primarily of a chronic nature. STELs are recommended only where toxic effects have been reported from high short-term exposures in either humans or animals. Exposures above the TLV-TWA up to the STEL should not be longer than 15 min and should not occur more than four times per day. There should be at least 60 min between successive exposures in this range. An averaging period other than 15 min may be recommended when this is warranted by observed biological effects.

Threshold limit value–time-weighted average (TLV-TWA). The TWA concentration for a conventional 8 h workday and a 40 h workweek, to which nearly all workers may be repeatedly exposed, day after day, without adverse effect.

Time-weighted average (TWA). An allowable exposure concentration averaged over a normal 8 h workday or a 40 h workweek.

Time-weighted average concentration (TWAC). The concentration of a substance to which a person is exposed in the ambient air, averaged over a period, usually 8 h.

Regarding units for some of the aforementioned terms, doses generally are expressed in terms of the quantity administered per unit body weight, quantity per skin surface area, or quantity per unit volume of the respired air. In addition, doses are also expressed over the duration of time that the dose was administered. Dose amounts are generally expressed as milligrams (one thousandth of one gram) per kilogram body weight (mg/kg). In some cases, grams per kilogram (g/kg), micrograms (one millionth of a gram) per kilogram ($\mu\text{g/kg}$), or nanograms (one billionth of a gram) per kilogram (ng/kg) are used. Volume measurements of dose can be converted to weight units by appropriate calculations. Densities can be obtained from standard reference texts. Where densities are not available, liquids are assumed to have a density of 1 g/mL. All body weights are converted to kilograms (kg) for uniformity. Concentrations of a gaseous substance in air are generally listed as parts of vapor or gas per million *by volume* (ppm_v). Concentrations of liquid or solid substances are usually expressed as parts per million *by weight or mass* (ppm_w or ppm_m). Other units include any mass per unit volume combination of units.

Illustrative Example 9.1

Convert concentration units to parts per million by volume (ppm_v) from mg/m^3 at a standard temperature and pressure of 0°C and 1.0 atm.

Solution

Set X as the concentration in mg/m^3 at 0°C and 1.0 atm. Apply the appropriate conversion factors:

$$\text{ppm}_v = X(\text{mg}/\text{m}^3)(1\text{m}^3/\text{L})(22.4\text{L}/\text{gmol})(\text{g}/10^3\text{mg})(\text{gmol}/\text{MW}(\text{g}));$$

MW = molecular weight, g/gmol

$$\text{ppm}_v = X[22.4/(10^6)(\text{MW})]$$

Thus, one notes that the conversion is *not* possible if the molecular weight (MW) of the gas is unknown.

Illustrative Example 9.2

Toxicological tests assess the effects of toxicants, including air toxicants, on animals, humans, microorganisms, or living cells. These tests have been used to determine the relative toxicity of various toxic compounds (including air toxins), i.e., categorizing chemicals in order from “extremely toxic” to “relatively harmless.” The dose and concentration of a toxicant that cause the deaths of exposed animals are represented by the LD₅₀ and LC₅₀ values, respectively. Explain the terms LD₅₀ and LC₅₀, and what routes of exposure are taken into consideration when conducting these toxicity tests.

Solution

Toxicological studies provide information on the response of organisms (animals, humans, microorganisms, or living cells) to toxicants.

The LD₅₀ (median lethal dose or lethal dose 50) is the single dose (in mg/kg) of a toxicant that will cause death in 50% of the exposed organisms over a specified observation period. The route of administration of the toxicant for conducting tests for obtaining the LD₅₀ value is oral, dermal, or parenteral (e.g., intravenous, subcutaneous, intramuscular) and is usually the first experiment performed with a new chemical. Different doses that are estimated to produce between 10% and 90% mortality are administered to test groups of animals. A dose–response curve is derived by plotting the chemical concentration given (dose) versus the death rate (response). The LD₅₀ is obtained from this curve using statistical procedures.

The LC₅₀ (median lethal concentration or lethal concentration 50) is the concentration (in parts per million) of a toxicant that will cause death in 50% of the exposed animals over a specified exposure and observation period. This test is generally used when the route of exposure is inhalation but is also used for aquatic toxicity testing when the exposure route is water. As with the LD₅₀, different concentrations that are estimated to produce between 10% and 90% mortality are administered to test groups of animals. A dose–response curve is generated and the LC₅₀ is obtained from this curve using statistical procedures.

Illustrative Example 9.3

Explain how the TWA is defined in equation form for a mixture of several contaminants.

Solution

TWA is the exposure standard for 8h exposure in Occupational Safety and Health Administration (OSHA) regulations for most chemical agents of concern. The describing equation is given by

$$TWA = \frac{\sum (C_i)(T_i)}{8h}$$

(9.1)

where
TWA is the time-weighted average concentration
C_i is the concentration of contaminant during the exposure period *i*
T_i is the time duration of corresponding period *i*

Illustrative Example 9.4

The TLV-TWA for a substance is 150 ppm_v. A worker begins a work shift at 8:00 AM and completes the shift at 5:00 PM. A 1 h lunch break is included between 12 noon and 1:00 PM, where it can be assumed that no exposure to the chemical occurs. Data were taken in the work area at the times indicated in Table 9.2. Has the worker exceeded the TLV specification?

Solution

Apply a modified form of Equation 9.1 as shown in Equation 9.2:

$$TWA = \frac{\sum C_i T_i}{\sum T_i}$$

(9.2)

TABLE 9.2
Time–Concentration Data for Illustrative
Example 9.4

Time	Concentration (ppm _v)	ΔT (h)	Average Concentration (ppm _v)
8:00	110		
9:00	130	1	C1 = 120
10:00	143	1	C2 = 137
11:00	162	1	C3 = 153
12:00	142	1	C4 = 152
1:00	157	0	C5 = 150
2:00	159	1	C6 = 158
3:00	165	1	C7 = 162
4:00	153	1	C8 = 159
5:00	130	1	C9 = 142

Substituting the values presented in Table 9.2 yields

$$\begin{aligned} TWA &= \frac{[(120)(1.0) + (137)(1.0) + (153)(1.0) + (152)(1.0) + (150)(0.0) \\ &\quad + (158)(1.0) + (162)(1.0) + (159)(1.0) + (142)(1.0)]}{8} \\ &= 148\text{ppm}_v \end{aligned}$$

9.3 Toxicology

Toxicology is the science of poisons, i.e., the study of chemical or physical agents that produce adverse responses in biological systems. Together with other scientific disciplines (such as epidemiology, i.e., the study of the cause and distribution of disease in human populations, and risk assessment), toxicology can be used to determine the relationship between an agent of interest and a group of people or a community. Of the many different types of toxicology (see Table 9.3), all of these different applications of the science start from a common nomenclature and set of cardinal principles.

Of interest to the engineer and scientist are the regulatory and environmental applications of the discipline. The former is of use in interpreting the setting of standards for allowable exposure levels of a given contaminant or agent in an ambient or occupational environment; the latter is of use in estimating the persistence and movement of an agent in a given environment. Both applications can be of direct use in risk assessment studies, and both regulatory toxicology and environmental toxicology closely

TABLE 9.3

Types of Toxicology

Type	Purpose
Clinical toxicology	To determine the effects of chemical poisoning and the treatment of poisoned people
Descriptive toxicology	To test the toxicity of chemicals
Environmental toxicology	To determine the environmental fate of chemicals and their ecological and health effects
Forensic toxicology	To answer medicolegal questions about health effects
Industrial toxicology	To determine health effects of occupational exposures
Mechanistic toxicology	To describe the biochemical mechanisms that cause health effects
Regulatory toxicology	To assess the risk involved in marketing chemicals and products and establish their subsequent regulation by government agencies

Source: Gute, D. and Hanes, N. *An Applied Approved to Epidemiology and Toxicology for Engineers*, NIOSH, Cincinnati, OH, 1993.

involve other branches of the discipline. The relationship is particularly close for the regulatory toxicologist who depends largely on the products of descriptive toxicology when making decisions on the risk posed by a specific agent.

There is a wide spectrum of doses among chemical agents needed to produce some adverse health effect. Although dose and exposure are sometimes used interchangeably, this is technically incorrect. As described earlier, the dose is the concentration or amount of an agent that becomes biologically available to the body at an anatomic site or target organ and that is capable of inducing an adverse health effect. Exposure, on the other hand, represents (in a very broad sense) the amount of the agent in the environment of concern. Exposure levels only translate to dose if the agent becomes available to the body through one of three principal routes of exposure: respiration, ingestion, or absorption through the skin. This is discussed in detail in Chapter 10.

Returning to dose, toxicologists employ quantitative measures of toxicity or the ability of an agent to cause some health effect. Health effects can range from minor skin irritation to something major such as death. A standard measure of toxicology employs death as the outcome. As described in the previous section, one measure is the dosage of an agent needed to produce death in 50% of the treated animals, LD_{50} , or the lethal dose. The primary sources of data for such measures are tests administered to laboratory animals, commonly mice and/or rats. Some chemicals considered extremely poisonous or toxic will achieve the LD_{50} with only a few micrograms of dose. Other agents will only cause harm if the host is challenged at large doses. The range of dose for some common agents is provided in Table 9.4. As noted earlier, most characterizations of dose are expressed as an amount relative to body weight, e.g., in mg/kg of body weight of the test

TABLE 9.4Approximate LD_{50} of Some Chemical Agents

Agent	LD_{50} (mg/kg)
Ethyl alcohol [2]	7060; rat 3450; mouse
Sodium chloride [3]	3000; rat
Morphine sulfate [4]	461; rat 600; mouse
Nicotine [2]	50; rat 3.34; mouse
Strychnine sulfate [2]	16; rat 2; mouse
Dioxin (TCDD) [5]	0.047; rat 0.114; mouse
Botulinum toxin [6]	0.0000004–0.0000012; mouse

animal. Thus, the LD_{50} attempts to answer the question, "How toxic is the compound or agent?"

Toxicity may also be viewed as a relative concept depending on the type and amount of the agent (dose). Toxicologists classify agents as to their toxicity by arranging all potential agents into categories based on the results of laboratory tests similar in nature to the LD_{50} results. The LD_{50} has an analog in the field of pharmacology where the effective dose for 50% of the test population, or ED_{50} , is routinely calculated for medicines. Categories for toxic agents range from practically nontoxic to extremely and super toxic, each with relevant specific dosages. It should also be noted that a good number of toxicological processes/effects are *reversible* over time.

A subset of toxicological factors can include lifestyle and environmental factors. Important lifestyle factors to be considered are smoking, alcohol and drug use, nutrition, sexual activity, personality, stress, economic/financial status, unemployment, mode of transportation, weight, education, occupation, sex, marital status, age, race, geographical location, recreational habits, etc. Environmental factors include air, water, and land pollution; food additives/contaminants; natural and/or man-made radiation; and one of the major topics addressed in this book—natural, domestic, and industrial accidents.

There are a number of ways in which chemicals can cause health effects. Some of the more common ways are listed in the following:

1. An *irritant* is an agent that causes health problems at the point of contact.
2. An *asphyxiant* is an agent that inhibits or restricts the oxygen supply to tissues.
3. *Central nervous system (CNS) depressants* act to interfere with brain or nervous system functions and generally suppress brain and/or motor activity.
4. Many agents are known to show or are suspected of showing *genetic activity*; this is generally the result of prolonged chronic exposure but may also occur through a one-time acute exposure and include:
 - *Carcinogenicity* refers to a property of some chemicals that increase the probability that cancer will develop at a later time as a result of an exposure.
 - *Mutagenicity* refers to a property of some chemicals which measure the probability that mutations will develop at a later time as a result of an exposure.
 - *Teratogenicity* refers to birth defects.

Physical stressors may also have to be considered in a health risk assessment. As noted in Chapter 8, these physical stressors can include:

1. Noise
2. Heat stress
3. Cold stress
4. Ultraviolet radiation
5. Ergonomics
6. Psychological injury
7. Psychological stress
8. Biological concerns

In conclusion, the purpose of a toxicity assessment is to weigh available evidence regarding the potential for particular contaminants to cause adverse effects in exposed individuals and to provide, where possible, an estimate of the relationship between the extent of exposure to a contaminant and the increased likelihood and/or severity of adverse effects. In the end, toxicological considerations are based on dose–response relationships.

Illustrative Example 9.5

Describe toxicology in layman terms.

Solution

As noted in this chapter, toxicology may be viewed as the “science of poisons,” where the term poison refers to a chemical that is capable of injuring or killing an organism. Alternately, one may describe it as the “study of harmful effects of chemicals.” Still others refer to it as the “study of a chemical’s ability to cause damage to the body.”

Illustrative Example 9.6

Describe the difference between human health evidence and inference.

Solution

Evidence is information measured directly, usually for individuals. Inference is information extrapolated from data that have been measured collectively from the general population.

9.4 Epidemiology

Epidemiology is a discipline within the health sciences that deals with the study of the occurrence of disease in human populations. The term is derived from the Greek words “Epi” (upon) and “Demos” (people) or

diseases upon people. Whereas physicians are generally concerned with a single patient, epidemiologists are generally concerned with groups of people who share certain characteristics. In effect, it attempts to employ previously observed outcomes (data) under real-world conditions to predict future (health) problems. A good example would be the interest epidemiologists show in characteristics associated with adverse health effects, i.e., smoking and lung cancer, asbestos exposure and asbestosis, or noise and hearing loss.

Epidemiology operates within the context of public health with a strong emphasis on the prevention of disease through the reduction of factors that may increase the likelihood that an individual or group will suffer a given disease. Implicit in the practice of epidemiology is the need for different disciplines in studying the influence of occupations on human health.

Epidemiological data come from many different sources. Acquiring reliable, accurate, and complete data describing occupational health problems is a key concern of the epidemiologist. A primary and continuing problem is the ascertainment of occupational disease and the transitional nature of some of the data. Ascertainment is the identification of diseases that are, in this case, of occupational origin.

Occupational disease is not a new phenomenon. Ample historical evidence exists recounting the effects of lead poisoning, chronic respiratory problems associated with mining, and hazards of manufacturing (including traumatic injury).

Although it has been known for a long time that occupational exposures can induce human disease, as in the aforementioned examples, the fact remains that diseases of occupational origin are underreported. This can be attributed to three major factors. The first is that health professionals generally do not gather enough information concerning the patient's occupational history or the various jobs and duties carried out by the patient to possibly link employment with his or her symptoms [7]. The second is that many of the diseases associated with occupational causes could have been caused by other risk factors. For example, the occupationally caused case of lung cancer does not appear with some distinct marker to differentiate it from a lung tumor caused by personal risk factors such as smoking. Exceptions do, of course, exist: mesothelioma—a relatively rare cancer of the lining of the lung—generally only occurs with exposure to asbestos. A third factor, particularly for chronic diseases, is the long-time interval that can exist between initial exposure to an occupational agent and the development of disease. This long-time interval can make the recognition of the occupational origin of a disease quite difficult. This is in stark contrast to the relative ease of associating physical injuries with job-related causes.

Latency refers to the period of time that elapses between the first contact of a harmful agent and a host and the development of identifiable symptoms or disease. Latency may be as short as a few hours, the time required for photochemical smog to induce watery eyes. Or it may stretch to 20–30 years for a

chronic condition such as asbestosis or malignant neoplasm of the lung. The association between a given exposure and a disease is all the more difficult because of the passage of time.

The types of epidemiological studies that attempt to note the number of cases of specific disease in a specific time period are generally known as *descriptive studies*. Descriptive studies attempt to provide investigators with information concerning the distribution of the disease in time and space as well as to identify attributes that may increase the chances of an individual contracting the disease. These attributes, called risk factors, include factors subject to change, such as physical inactivity, as well as those that are immutable, such as gender or age. For example, well-established risk factors for occupationally induced lung cancer include asbestos and coke oven emissions. Descriptive studies are also helpful in the formation of hypotheses regarding exposure and disease. Studies seeking to prove or disprove specific hypotheses are called *analytical studies*. The two basic types of analytical studies are the *cohort* and the *case–control* study. Each has strengths and weaknesses as well as different resource and time requirements. These are briefly discussed below.

The *cohort* study involves the study of individuals classified by exposure characteristics, e.g., a group of welders. The study then follows the development of disease in the welders' group as well as in an unexposed comparison population. The measure that assesses the magnitude of association between the exposure and the disease and that which indicates the likelihood of developing the disease in the exposed group relative to the unexposed is the relative risk. A relative risk of 1.0 indicates no difference between the disease experience in the two groups. A relative risk of greater than 1.0 indicates a positive association between the exposure and the disease and an increased risk in those who are subject to the exposure.

In the *case–control* design, a group with a disease (cases) is compared with a selected group of nondiseased (control) individuals with respect to exposure. The relative risk in control studies can only be estimated as the incidence rate among exposed individuals cannot be calculated. The estimator used is the odds ratio, which is the ratio of the odds of exposure among the cases to that among the controls.

The main difference between the case–control and the cohort type of study is that in the case–control format, the investigator begins by classifying study subjects as to disease status. With the cohort study, the investigator begins by separating study subjects by exposure status. There are major resource consumption differences between the types of study. Cohort studies generally consume more resources and take longer to complete than do case–control studies.

A pressing challenge for epidemiologists interested in occupational health is to derive an accurate picture of disease frequency. This challenge is met by two broad types of measurements: *prevalence* and *incidence*. These are briefly described below.

Disease refers to the number of cases existing in a population. Point prevalence identifies the prevalence estimated at a given time, e.g., the number of workers with abnormal chest films from a survey. Prevalence is computed as the number of cases divided by the number of study subjects at a given point in time:

$$\text{Prevalence} = \frac{\text{Number of persons with a disease}}{\text{Total number in the study}} \quad (9.3)$$

Prevalence is thus not a true rate but simply a proportion, although the term prevalence rate is used.

Incidence, a true rate, refers to the number of new cases of a disease in a defined population in a given period of time. Thus, the incidence rate can be expressed as

$$\text{Incidence rate} = \frac{\text{Number of new cases of disease during time period}}{\text{Total number at risk}} \quad (9.4)$$

Central to epidemiology is the use of rates to express the health experience of populations. Rates are important because epidemiology is inherently a comparative discipline. An epidemiologist is constantly attempting to compare the disease experience of a study population with that of a comparison population. A rate is nothing more than a specialized proportion in which the counts of people with a particular disease are placed over a denominator that is composed of people who are at risk, i.e., who have a chance of developing the disease. Men, for example, would not be included in the denominator used to calculate the prevalence or incidence of uterine cancer.

To summarize, epidemiology is concerned with studies related to health problems in society and the application of this information to eliminate, reduce, and/or control health-related and death-related issues. The studies can involve

1. Experiments
2. Surveillance
3. Simple or detailed observations
4. Standard statistical analysis
5. Hypothesis testing

Documenting the physical, social, cultural, behavioral, biological, etc., factors discussed earlier is usually an integral part of the studies.

Illustrative Example 9.7

Briefly describe the difference between toxicology and epidemiology.

Solution

Toxicology deals with the adverse effects of chemical substances on living things. Most of the information on toxic effects of chemicals in humans provided by toxicology is derived from animal studies. Epidemiology analyzes the relationship between a chemical and the disease in an exposed population. Information on toxic effects of chemicals in humans provided by epidemiology is derived from direct human evidence.

Illustrative Example 9.8

Ten new cases of a strange ailment experienced by U.S. women using a face cream containing nanoparticles during the 2011 calendar year were reported. It was previously estimated that 1,325,000 people used the cream. Calculate the incidence rate (IR) of this face cream–related ailment.

Solution

Based on the problem statement and applying Equation 9.4 yields

$$IR = \frac{10}{1,325,000} = 7.55 \times 10^{-6}$$

The reader should note once again that epidemiology uses ratios to express the health experience of populations. Ratio increases in reported problems over an extended period of time can potentially lead to misleading results. For example, if the number of problems increased from 10 to 40 over a 3 year period, one could be (incorrectly) led to believe the average percent increase per year was 100%. If this were true, there would be 20 problems after Year 1, 40 problems after Year 2, and 80 problems after Year 3. The correct approach for an increase from P to F over an M year period is given by

$$F = P(1 + i)^M \quad (9.5)$$

where i is the average percent (on a fractional basis) increase. For the aforementioned case, $i = 0.59$ or 59%.

9.5 Noncarcinogens

This section summarizes how health effects information is considered in the toxicity assessment for noncarcinogenic effects [8]. The RfD is the toxicity

value used most often in evaluating noncarcinogenic effects. The methods the EPA uses for developing RfDs were presented earlier but are described again because of the number of different RfDs. Various types of RfDs are available depending on the exposure route (oral or inhalation), the critical effect (developmental or other), and the length of exposure being evaluated (chronic, subchronic, or single effect).

A chronic RfD is defined as an estimate (with an uncertainty spanning perhaps an order of magnitude or greater) of a daily exposure level for the human population, including sensitive subpopulations, that is likely to be without an appreciable risk of deleterious effects during a lifetime. Chronic RfDs are specifically developed to be protective for long-term exposure to a compound. As a guideline for Superfund program risk assessments, chronic RfDs generally are often used to evaluate the potential noncarcinogenic effects associated with exposure periods between 7 years (approximately 10% of a human lifetime) and a lifetime. Many chronic RfDs have been reviewed and verified by an intra-agency RfD Workgroup and entered into the EPA's IRIS.

The EPA has developed subchronic RfDs (RfD_{ss}), which were earlier useful for characterizing potential noncarcinogenic effects associated with shorter-term exposures, and developmental RfD_{ds} , which are useful specifically for assessing potential developmental effects resulting from exposure to a compound. For example, as a guideline for Superfund program risk assessments, subchronic RfDs should be used to evaluate the potential noncarcinogenic effects of exposure periods between 2 weeks and 7 years. Such short-term exposures can result when a particular activity is performed for a limited number of years or when a chemical with a short half-life degrades to negligible concentrations within several months to several years. Developmental RfDs are used to evaluate the potential effects on a developing organism following a single exposure event.

9.5.1 Concept of Threshold

For many noncarcinogenic effects, protective mechanisms are believed to exist that must be overcome before the adverse effect is manifested. For example, where a large number of cells perform the same or similar function, the cell population may have to be significantly depleted before the effect is seen. As a result, a range of exposures exists from zero to some finite value that can be tolerated by the organism with essentially no chance of an expression of adverse effects. In developing a toxicity value for evaluating noncarcinogenic effects (i.e., an RfD), the approach is to identify the upper bound of this tolerance range (i.e., the maximum sub-threshold level). Because variability exists in the human population, attempts are made to identify a sub-threshold level protective of sensitive individuals in the population. For most chemicals, this level can only be estimated; the RfD

incorporates uncertainty factors (UFs) indicating the degree or extrapolation used to derive the estimated value. RfD summaries in IRIS also contain a statement expressing the overall confidence (high, medium, or low) that the evaluators have in the RfD. The RfD is generally considered to have an uncertainty spanning an order of magnitude or more, and therefore the RfD should not be viewed as a strict scientific demarcation between what dose is toxic and what is nontoxic.

9.5.2 Derivation of an Oral RfD

In the development of oral RfDs, all available studies examining the toxicity of a chemical following exposure by the oral route are gathered and judged for scientific merit. Occasionally, studies based on other exposure routes (e.g., inhalation) are considered, and the data are adjusted for application via the oral route. Any differences between studies are reconciled and an overall evaluation is reached. If adequate human data are available, this information is used as the basis for the RfD. Otherwise, animal study data are used. In these cases, a series of professional judgments are made that involve, among other considerations, an assessment of the relevance and scientific quality of the experimental studies. If data from several animal studies are being evaluated, the EPA first seeks to identify the animal model that is most relevant to humans based on a defensible biological rationale, e.g., using comparative metabolic data. In the absence of a species that is clearly the most relevant, the EPA assumes that humans are at least as sensitive to the substance as the most sensitive animal species tested. Therefore, as a matter of science policy, the study on the most sensitive species (the species showing a toxic effect at the lowest administered dose) is selected as the critical study for the basis of the RfD. The effect characterized by the LOAEL after accurate conversions, to adjust for species differences, is referred to as the *critical toxic effect*.

After the critical study and toxic effect have been selected, the EPA identifies the experimental exposure level representing the highest level tested at which no adverse effects (including the critical toxic effect) were demonstrated. This highest NOAEL is the key datum obtained from the study of the dose–response relationship. A NOAEL observed in an animal study in which the exposure was intermittent (such as 5 days/week) is adjusted to reflect continuous exposure.

The NOAEL is selected based, in part, on the assumption that if the critical toxic effect is prevented, then all toxic effects are prevented. The NOAEL for the critical toxic effect should not be confused with the NOEL. In some studies, only a LOAEL rather than a NOAEL is available. The use of a LOAEL, however, requires the use of an additional UF (as discussed later).

The RfD is derived from the NOAEL (or LOAEL) for the critical toxic effect by consistent application of UFs and an MF. The UFs generally consist of

multiples of 10 (although values less than 10 are sometimes used), with each factor representing a specific area of uncertainty inherent in the extrapolation from the available data. The bases for application of different UFs are as follows:

1. A UF of 10 is used to account for variation in the general population and standards are intended to protect sensitive subpopulations (e.g., the elderly and children).
2. A UF of 10 is used when extrapolating from animals to humans. This factor is intended to account for the interspecies variability between humans and other mammals.
3. A UF of 10 is used when a NOAEL derived from a subchronic instead of a chronic study is used as the basis for a chronic RfD.
4. A UF of 10 is used when a LOAEL is used instead of an NOAEL. This factor is intended to account for the uncertainty associated with extrapolating from LOAELs to NOAELs.
5. In addition to the UFs listed earlier, an MF is also applied. An MF ranging from >0 to 10 is included to reflect a qualitative professional assessment of additional uncertainties in the critical study and in the entire database for the chemical not explicitly addressed by the preceding UFs. The default value for the MF is 1.0.

To calculate the RfD, the appropriate NOAEL (or the LOAEL if a suitable NOAEL is not available) is divided by the product of all of the applicable UFs and the MF as presented in Equation 9.6:

$$RfD = \frac{NOAEL \text{ or } LOAEL}{(UF_1 \times UF_2 \times \cdots \times MF)} \quad (9.6)$$

Oral RfDs typically are expressed as one significant figure in units of mg/kg-day.

9.5.3 Derivation of an Inhalation RfD

The methods the EPA uses in the derivation of inhalation RfDs (RfD_i s) are similar in concept to those used for oral RfDs; however, the actual analysis of inhalation exposures is more complex than oral exposures due to:

1. The dynamics of the respiratory system and its diversity across species
2. Differences in the physiochemical properties of contaminants

Although the identification of the critical study and the determination of the NOAEL in theory are similar for oral and inhalation exposures, several important differences should be noted. In selecting the most appropriate study, the EPA considers differences in respiratory anatomy and physiology, as well as differences in the physicochemical characteristics of the contaminant. Differences in respiratory anatomy and physiology may affect the pattern of contaminant deposition in the respiratory tract and the clearance and redistribution of the agent. Consequently, different species may not receive the same dose of the contaminant at the same locations within the respiratory tract even though both species were exposed to the same particle or gas concentration. Differences in the physicochemical characteristics of the contaminants, such as the size and shape of a particle or whether the contaminant is an aerosol or a gas, also influence deposition, clearance, and redistribution.

In inhalation exposures, the target tissue may be a portion of the respiratory tract or, if the contaminant can be absorbed and distributed through the body, some extrapulmonary organ. Because the pattern of deposition may influence concentrations at different tissues of the lung, the toxic health effect observed may be more directly related to the pattern of deposition than to the exposure concentration. Consequently, the EPA considers the deposition, clearance mechanisms, and the physicochemical properties of the inhaled agent in determining the effective dose delivered to the target organ.

Doses calculated in animals are converted to equivalent doses in humans on the basis of comparative physiological considerations (e.g., ventilatory parameters and regional lung surface areas). Additionally, if the exposure period is discontinuous, it is adjusted to reflect continuous exposure.

The inhalation RfD is derived from the NOAEL by applying UFs similar to those listed earlier for oral RfDs. A UF of 10 is used when extrapolating from animals to humans in addition to the calculation of the human equivalent dose to account for interspecific variability in sensitivity to the toxicant. The resulting RfD value for inhalation exposure is generally reported as a concentration in air in mg/m^3 for continuous, 24 h/day exposure, although it may be reported as a corresponding inhaled intake (in $\text{mg}/\text{kg}\cdot\text{day}$). A human body weight of 70 kg and an inhalation rate of $20 \text{ m}^3/\text{day}$ are used to convert between an inhaled intake expressed in units of $\text{mg}/\text{kg}\cdot\text{day}$ and a concentration in air expressed in mg/m^3 .

9.5.4 Derivation of a Subchronic RfD

The chronic RfDs described earlier pertain to lifetime or other long-term exposures and may be overly protective if used to evaluate the potential for adverse health effects resulting from substantially less-than-lifetime exposures. For such situations, the EPA has begun calculating toxicity values

specifically for subchronic exposure durations, using a method similar to that outlined earlier for chronic RfDs. The EPA's Environmental Criteria and Assessment Office and EPA's Superfund Program develop subchronic RfDs and, although they have been peer reviewed by agency and outside reviewers, subchronic RfDs values have not undergone verification by an intra-agency workgroup. As a result, subchronic RfDs are considered interim rather than verified toxicity values and are only used for subchronic-to-chronic extrapolation placed in IRIS.

Development of subchronic RfDs parallels the development of chronic RfDs in concept; the distinction is one of exposure duration. Appropriate studies are evaluated and a subchronic NOAEL is identified. The RfD is derived from the NOAEL by the application of the UFs and an MF, as outlined earlier. When experimental data are available only for shorter exposure durations than desired, an additional UF is applied. This is similar to the application of the UF for duration differences when a chronic RfD is estimated from subchronic animal data. On the other hand, if subchronic data are missing and a chronic oral RfD derived from chronic data exists, the chronic oral RfD is adopted as the subchronic oral RfD. In this instance, there is no application of a UF to account for differences in exposure duration.

9.5.5 Derivation of Developmental Toxicant RfD

In developing a developmental toxicant RfD (RfD_{dt}), evidence is gathered regarding the potential of a substance to cause adverse effects in a developing organism as a result of exposure prior to conception (either parent), during prenatal development, or postnatally prior to the time of sexual maturation. Adverse effects can include death, structural abnormalities, altered growth, and functional deficiencies. Maternal toxicity is also considered. The evidence is assessed, and the substance is assigned a weight-of-evidence designation according to a specific scheme. In this scheme, three levels are used to indicate the assessor's degree of confidence in the data: definitive evidence, adequate evidence, and inadequate evidence. The definitive and adequate evidence categories are subdivided as to whether the evidence demonstrates the occurrence or the absence of adverse effects.

After the weight-of-evidence designation is assigned, a study is selected for the identification of an NOAEL. The NOAEL is converted to an equivalent human dose, if necessary, and divided by UFs similar to those used in the development of an oral RfD. It should be remembered that the RfD_{dt} is based on a short duration of exposure because even a single exposure at a critical time (e.g., during gestation) may be sufficient to produce adverse developmental effects and that chronic exposure is not a prerequisite for developmental toxicity to be manifested. Therefore, RfD_{dt} values are appropriate for evaluating single event exposures, which usually are not adjusted based on the duration of exposure.

9.5.6 Calculation Scheme for Noncarcinogens

The preliminary assessment of noncarcinogenic risk associated with a hazardous waste site as recommended by the EPA is typically calculated in four major steps [9].

1. Identify discrete exposure conditions:
 - a. Exposure route
 - b. Frequency
 - c. Duration
 - d. Administered dose
2. Derive appropriate RfDs for each discrete set of conditions.
3. Evaluate the hazard for noncarcinogenic effects as a ratio of exposure dose to the recommended RfD.
4. Aggregate the hazard for multiple chemical agents and exposure pathways as a hazard index (HI) where appropriate.

The ratio referred to in the third step is utilized to quantify risk from noncarcinogens. As the fourth step indicates, the HI for individual chemicals may be summed for chemicals affecting a particular target organ or acting by a common mechanism in order to provide a final measure of overall or cumulative noncarcinogenic toxic risk. If the sum of HIs is less than 1, then the risk of adverse health effects is considered acceptable.

9.5.7 Dose–Response Relationships

The dose–response relationship defines the potential problem associated with a chemical and represents the heart of most toxicological studies. A dose–response relationship is presented between a chemical and an effect (response) when, as the concentration of the chemical at the reactive site increases, the probability that the effect or response in the receptor also increases. It should be noted the receptor can represent an (one) individual or a population (number of individuals). A characteristic dose–response curve is presented in Figure 9.1. A threshold would exist if there was a level of dose for which no apparent adverse effect would be discerned from exposure to chemicals as presented in Figure 9.2. As noted earlier, this is a strongly debated topic for carcinogens. The regulatory community, in the interests of protecting the health of the public, usually assumes that *no threshold* exist for carcinogenic compounds. This is discussed further in the next section.

It should be noted that dose–response information is generally extended via an extrapolation of data obtained from high doses administered to test animals to levels expected from human contact. In effect, the rationale employed is based on low-dose extrapolation since it is not usually possible to obtain meaningful data from animal studies conducted at low doses.

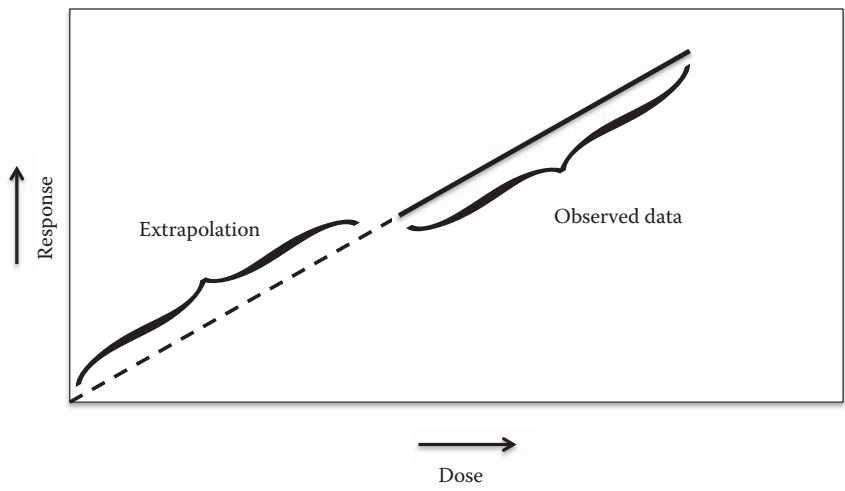


FIGURE 9.1
Characteristic dose–response curve.

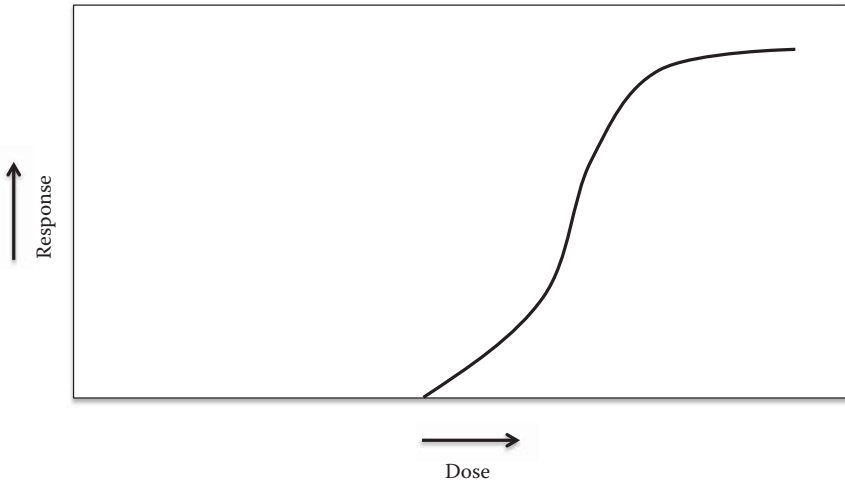


FIGURE 9.2
Dose–response curve containing a threshold.

9.6 Carcinogens

This section describes how the types of toxicity information are considered in the toxicity assessment for carcinogenic effects. A *slope factor* and the accompanying *weight-of-evidence* determination are the data most commonly

used to evaluate potential human carcinogenic risks. The methods the EPA uses to derive these values are outlined below.

9.6.1 Concept of Nonthreshold Effects

Carcinogenesis, unlike many noncarcinogenic health effects, is generally thought to be a phenomenon for which risk evaluation based on the presumption of a threshold is inappropriate. For carcinogens, the EPA assumes that a small number of molecular events can evoke changes in a single cell that can lead to uncontrolled cellular proliferation and eventually to a clinical state of the disease. This hypothesized mechanism for carcinogenesis is referred to as “nonthreshold” because there is believed to be essentially no level of exposure to such a chemical that does not pose a finite probability of generating carcinogenic effects. However, the concept of nonthreshold for carcinogens continues to be questioned.

The EPA uses a two-part evaluation in which the substance first is assigned a weight-of-evidence classification, and then a slope factor is calculated.

9.6.2 Assigning a Weight of Evidence

In assigning a weight of evidence, the available data are evaluated to determine the likelihood that the agent is a human carcinogen. The evidence is characterized separately for human studies and animal studies as sufficient, limited, inadequate, no data, or evidence of no effect. The characterizations of these two types of data are combined, and based on the extent to which the agent has been shown to be a carcinogen in experimental animals or humans, or both, the agent is given a provisional weight-of-evidence classification. EPA scientists then adjust the provisional classification upward or downward, based on other supporting evidence of carcinogenicity.

The EPA classification system for weight of evidence is shown in Table 9.5. This system is adapted from the approach taken by the International Agency

TABLE 9.5

EPA Weight-of-Evidence Classification System for Carcinogenicity Assessment

Class	Description
A	Human carcinogen
B1 or B2	Probable human carcinogen
B1	Indicates that limited human data are available
B2	Indicates sufficient evidence in animals and inadequate or no evidence in human
C	Possible human carcinogen
D	Not classifiable as to human carcinogenicity
E	Evidence of noncarcinogenicity for humans

for Research on Cancer (IARC) and classifies carcinogens into Classes A, B1, B2, C, D, and E as defined in Table 9.5. For example, the EPA utilizes the following description for Group A—Human Carcinogens: [Compounds for which] “... there is sufficient evidence from epidemiologic studies to support a causal association between exposure to the agent and cancer.” This designation is based on the weight of evidence, and, therefore, the designation as a human carcinogen represents a consensus opinion with an expert group rather than a scientific fact.

9.6.3 Generating a Slope Factor

A slope factor is generated in the second part of the evaluation [10]. Based on the evaluation that the chemical is a known or probable human carcinogen, a toxicity value that defines quantitatively the relationship between dose and response (i.e., the slope factor) is calculated. Slope factors are typically calculated for potential carcinogens in Classes A, B1, and B2. Quantitative estimation of slope factors for the chemicals in Class C proceeds on a case-by-case basis.

Generally, the slope factor is a plausible upper bound estimate of the probability of a response per unit intake of a chemical over an average lifetime. The slope factor is used in risk assessments to estimate an upper-bound lifetime probability of an individual developing cancer as a result of exposure to a particular level of a potential carcinogen. Slope factors should always be accompanied by the weight-of-evidence classification to indicate the strength of the evidence that the agent is a human carcinogen.

9.6.4 Identifying the Appropriate Data Set

In deriving slope factors, the available information about a chemical is evaluated and an appropriate data set is selected. In choosing appropriate data sets, human data of high quality are preferable to animal data. If animal data are used, the species that responds most similarly to humans (with respect to factors such as metabolism, physiology, and pharmacokinetics) is preferred. When no clear choice is possible, the most sensitive species is given the greatest emphasis. Occasionally, in situations where no single study is judged most appropriate, yet several studies collectively support the estimate, the geometric mean of estimates from all studies may be adopted as the slope factor. This practice ensures the inclusion of all relevant data.

Because risk at low exposure levels is difficult to measure directly either by animal experiments or by epidemiological studies, the development of a slope factor generally entails applying a model to the available data set and using the model to extrapolate from the relatively high doses administered to experimental animals (or the exposures noted in epidemiological studies) to the lower exposure levels expected for human contact in the environment.

A number of mathematical models and procedures have been developed to extrapolate from carcinogenic responses observed at high doses to responses expected at low doses. Different extrapolation methods may provide a reasonable fit to the observed data but may lead to large differences in the projected risk at low doses. The choice of a low-dose extrapolation model is governed by consistency with current understanding of the mechanism of carcinogenesis and not solely on goodness of fit to the observed tumor data. When data are limited and when uncertainty exists regarding the mechanisms of carcinogenic action, the EPA guidelines suggest that models or procedures that incorporate low-dose linearity are preferred when compatible with the limited information available. The EPA's guidelines recommend that the linearized multistage model be employed in the absence of adequate information to the contrary.

In general, after the data are fit to the appropriate model, the upper 95% confidence limit of the slope of the resulting dose–response curve is calculated. This value is known as the slope factor and represents an upper 95% confidence limit on the probability of a response per unit intake of a chemical over a lifetime (i.e., there is only a 5% chance that the probability of a response could be greater than the estimated value on the basis of the experimental data and model used). In some cases, slope factors based on human dose–response data are based on the “best” estimate instead of the upper 95% confidence limits. Because the dose–response curve generally is linear only in the low-dose region, the slope factor estimate only holds true for low doses. Information concerning the limitations on use of slope factors can be found in IRIS.

Because of limited epidemiological data, most of the understanding about the potential for a toxic substance to cause cancer is based on animal testing. Substances not having an apparent epidemiological association with human cancer but which have induced cancer in test animals are referred to as *potential* human carcinogens. Several hundred substances for which there is inadequate human epidemiological data have been assigned as potential human carcinogens based upon testing data in laboratory animals, usually rats and mice.

When animal data are used as a basis for extrapolation, the human dose that is equivalent to the dose in the animal study is calculated using the assumption that different species are equally sensitive to the effects of a toxicant if they absorb the same amount of the agent per unit of body surface area. This assumption is made only in the absence of specific information about the equivalent doses for the chemical in question. Because surface area is approximately proportional to the two-third power of body weight, the equivalent human dose (in mg/day, or other units of mass per unit time) is calculated by multiplying the animal dose (in identical units) by the ratio of human to animal body weights raised to the two-third power. For animal doses expressed as mg/kg-day, the equivalent human dose, in the same units, is calculated by multiplying the animal dose by the ratio of animal to human body weights raised to the one-third power.

When using animal inhalation experiments to estimate lifetime human risks for partially soluble vapors or gases, the air concentration (ppm_v) is generally considered to be the equivalent dose between species based on equivalent exposure times (measured as fractions of a lifetime). For inhalation of particulates or completely absorbed gases, the amount absorbed per unit of body surface area is considered to be the equivalent dose between species.

Toxicity values for carcinogenic effects can be expressed in several ways. As discussed earlier, the slope factor is usually, but not always, the upper 95% confidence limit of the slope of the dose–response curve and is expressed as $(\text{mg}/\text{kg}\text{-day})^{-1}$. If the extrapolation model selected is the linearized multi-stage model, this value is also known as the q_1 . Equation 9.7 describes this relationship:

$$\text{Slope factor} = \text{Risk per unit dose} = \text{Risk per mg/kg-day} \quad (9.7)$$

Where data permit, slope factors listed in IRIS are based on absorbed doses, although many of them to date have been based on administered doses.

Toxicity values for carcinogenic effects also can be expressed in terms of risk per unit concentration of the substance in the medium where human contact occurs. These measures, called unit risks, are calculated by dividing the slope factor by 70 kg and multiplying by the inhalation rate ($20 \text{ m}^3/\text{day}$) or the water consumption rate (2 L/day), respectively, for risk associated with unit concentration in air or water. See Equations 9.8 and 9.9. Where an absorption fraction of less than 1.0 has been applied in deriving the slope factor, an additional conversion factor is necessary in the calculation of unit risk so that the unit risk will be on an administered dose basis. The standardized duration assumption for unit risks is understood to be continuous lifetime exposure. Hence, when there is no absorption conversion required,

$$\text{Air unit risk} = \text{Risk per } \mu\text{g}/\text{m}^3 = (\text{Slope factor})(1/70 \text{ kg})(20 \text{ m}^3/\text{day})(10^{-3}) \quad (9.8)$$

$$\text{Water unit risk} = \text{Risk per } \mu\text{g}/\text{L} = (\text{Slope factor})(1/70 \text{ kg})(2 \text{ L/day})(10^{-3}) \quad (9.9)$$

The multiplication by 10^{-3} is necessary to convert from mg (the slope factor is given in $[\text{mg}/\text{kg}\text{-day}]^{-1}$) to μg (the unit risk is given in $[\mu\text{g}/\text{m}^3]^{-1}$ or $[\mu\text{g}/\text{L}]^{-1}$).

The number of strictly human epidemiological studies is small. A total of approximately 50 compounds (e.g., benzene, vinyl chloride) and complex mixtures (e.g., aluminum production, tobacco smoke) have sufficient data available to permit their classification as human carcinogens [11]. The most potent human carcinogens known, the aflatoxins, are of natural origin.

Their presence in food products through infestation by toxin-producing fungi constitutes a serious problem in several tropical and subtropical countries.

9.6.5 Dose–Response Relationships

To predict the likely outcome from human exposure to carcinogenic chemicals, the development of dose–response relationships is necessary. To develop these relationships, toxicologists ordinarily depend upon animal data. A typical dose–response curve in the high dose region is given in Figure 9.3 for a hypothetical carcinogen. The approach to developing dose–response relationships for carcinogens differs somewhat from the approach for non-carcinogens. For ease of comparison, doses (the abscissa) are almost always plotted as the daily administered dose per unit of body weight (mg/kg-day). Dose is plotted against response (the ordinate), which is the incidence of the total number of tested animals with tumors (dimensionless). Figure 9.3 represents the best fit of mean values. It should be noted that the ordinate is reported as excess incidences of cancer or the incidence in the exposed animals minus the normal spontaneous (background) incidence in the control population.

When assessing lifetime cancer risk to humans, it is widely accepted that carcinogenesis works in a manner such that it is possible, however remote,

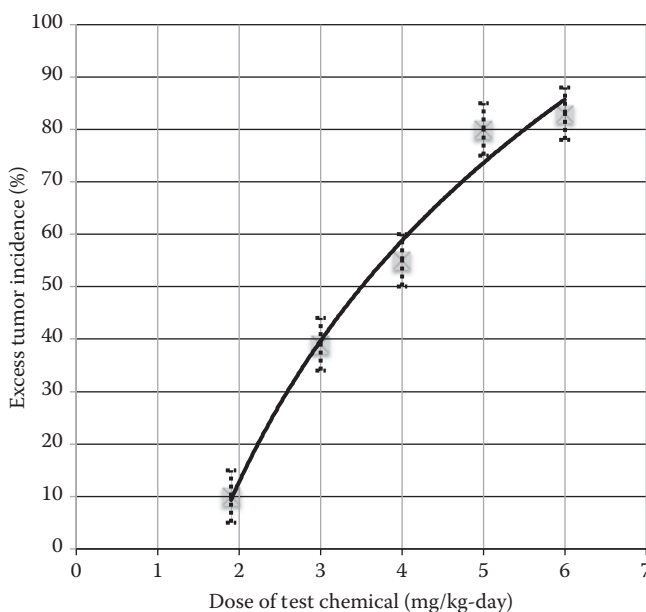


FIGURE 9.3

Hypothetical dose–response curve for a typical carcinogen.

that exposure to a single molecule of a genotoxic carcinogen could result in one of the two mutations necessary to initiate cancer (i.e., genotoxins do not exhibit thresholds). In theory, therefore, the dose–response curve is asymptotic to “zero” incidence. Because there is no threshold, there is no safe level, only “acceptable levels.” The public has expressed concern with any level, but regulatory agencies tend to establish a regulatory goal of one-in-one million (1×10^{-6} or 0.0001%) excess lifetime cancer risk.

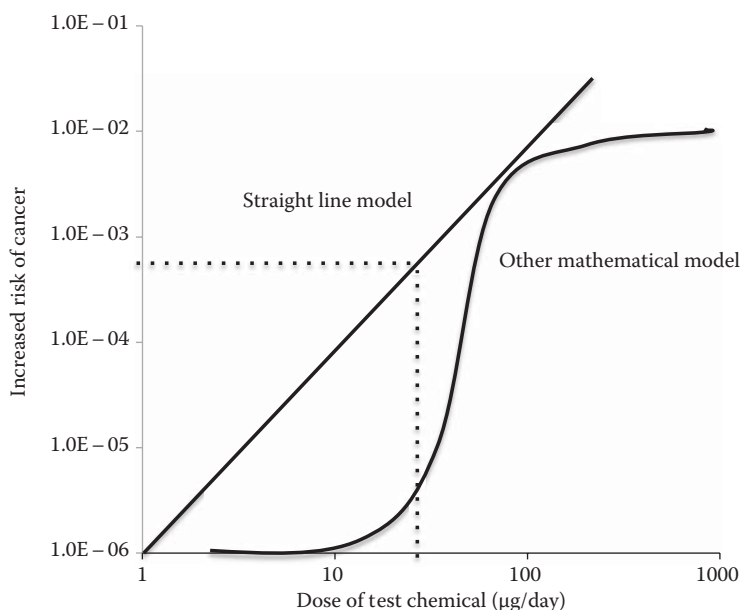
As stated before, it is not practical to test in the range of such a low incidence. In fact, laboratories conduct animal tests at high doses to increase the likelihood of inducing a measureable cancer incidence in a portion of a test population. Thus, to apply the results of animal tests to human exposures, the data from the high doses used in the tests must be extrapolated to the low doses of public concern.

The calculation of carcinogenic risk involves the use of a CPF. A CPF is the slope of the dose–response curve at very low exposures and is now referred to as slope factor. The dimensions of a CPF, or a slope factor, are expressed as the inverse of daily dose (mg/kg-day)⁻¹. Having derived a CPF, the calculation of carcinogenic risk is straightforward. Quantification of carcinogenic risk of an exposure simply requires converting the dose to appropriate terms (mg/kg-day) and multiplying it by the slope factor.

Illustrative Example 9.9

As noted earlier, a dose–response relationship provides a mathematical formula or graph for estimating a person’s risk of illness at each exposure level for human toxins. To estimate a dose–response relationship, measurements of health effects are needed for at least one dose level of the toxic agent compared to an unexposed group. However, there is one important difference between the dose–response curve commonly used for estimating the risk of cancer and the ones used for estimating the risk of all other illnesses: the existence of a threshold dose, that is, the aforementioned highest dose at which there is no risk of illness for the noncarcinogenic risk. Because a single cancerous cell may be sufficient to cause a clinical case of cancer, EPA’s and many others’ dose–response models for cancer assume that the threshold dose level for cancer is zero. In other words, people’s risk of cancer is increased even at very low doses. However, the increased cancer risk at very low doses is likely to also be very low.

Draw a straight-line model showing the level of cancer risk increasing at a constant rate as the dose level increases. The model should illustrate increasing risk of cancer for the toxic agent. (It is accepted by scientists that the human body is capable of adjusting to varying amounts of cell damage without showing signs of illness. Therefore, the EPA has developed models for noncancer illnesses that include a threshold dose level that is greater than zero; this means that at low doses, there may be no risk of adverse health effects. For noncancer health effects, such as permanent liver or kidney damage, temporary skin rashes, or asthma

**FIGURE 9.4**

Cancer dose–response curve highlighting the straight line dose response model.

attacks, information from human or animal studies is used to estimate the threshold dose levels).

Solution

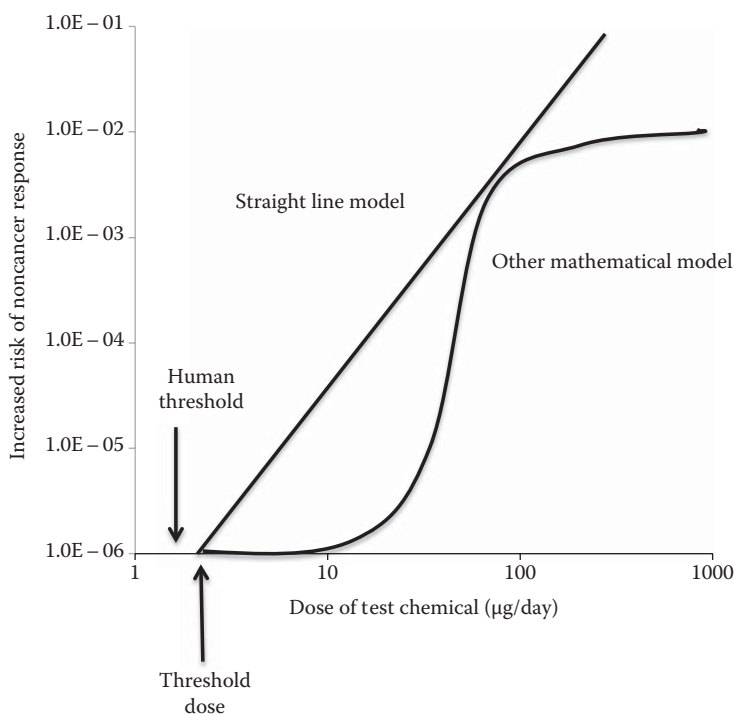
Figure 9.4 shows the cancer dose–response curve plotted from data on a dose of $100\text{ }\mu\text{g/d}$. This dose caused an extra chance of cancer of about 1 in 100 in the study animals that received the dose. The straight-line model developed here indicates that the level of cancer risk increases at a constant rate as the dose level increases, and this rate of increasing cancer risk is known as the slope factor for the toxic agent.

Illustrative Example 9.10

With reference to non-cancer health effects develop a straight-line model to show the EPA's methodology in which the EPA adjusts the observed threshold from animal studies downward to the human threshold by dividing by UFs that range from 1 to 10,000.

Solution

Figure 9.5 illustrates the noncancer dose–response curve, which was drawn after converting uncertainties from animal to human data. Since individuals vary in their susceptibility to the harmful effects of toxic agents, EPA adjusts the observed threshold dose downward by dividing

**FIGURE 9.5**

Noncancer dose–response curve highlighting the straight line dose–response model and the threshold dose.

by UFs that range from 1 to 10,000. This new adjusted value is known as the human threshold at which EPA expects no appreciable risk of harmful health effects for most of the general population. This example shows the application of a UF of approximately 2 to animal threshold dose results.

9.7 Uncertainties/Limitations

Once again, the subject of uncertainties is revisited. It is important to keep in mind that statistically based studies by themselves can never prove the existence of a cause and effect relationship. However, such observations may be used to generate or to test a hypothesis. Many possibilities exist for introducing bias in health risk investigations, and statistical correlations may be fortuitous. It is, therefore, of utmost importance that any such correlation or conclusion be supported by a biological plausibility based on existing toxicology data and other information. Here, common sense is a logical first step. Even for the case of a well-established cause and effect relationship,

confounding factors can often impede the establishment of a reliable dose–response (effect) relationship [12].

For a variety of reasons, it is difficult to precisely evaluate toxic responses caused by exposures (particularly acute ones) to hazardous chemicals. Some issues related to precise prediction of these toxic responses in human populations are noted in the following:

1. Humans experience a wide range of acute adverse health effects, including irritation, narcosis, asphyxiation, sensitization, blindness, organ system damage, and death. In addition, the severity of many of these effects varies with intensity and duration of exposure. For example, exposure to a substance at an intensity that is sufficient to cause only mild throat irritation is of less concern than one that causes severe eye irritation, lacrimation, or dizziness, since the latter effects, for example, are likely to impede escape from the area of contamination.
2. There is a high degree of variation in response among individuals in a typical population. Generally, sensitive populations include the elderly, children, and individuals with diseases that compromise the respiratory or cardiovascular system.
3. For the overwhelming majority of substances encountered in industry, there are not enough data on toxic responses of humans to permit an accurate or precise assessment of the substance's hazard potential. Frequently, the only data available are from controlled experiments conducted with laboratory animals. In such cases, it is necessary to extrapolate from effects observed in animals to effects likely to occur in humans. Thus, extrapolation requires the professional judgment of a toxicologist.
4. Many releases involve multicomponents. There are presently only "guidelines" on how these types of releases should be evaluated [13]. Are they additive, synergistic, or antagonistic in their effects on receptors? As more information is developed on the characterization of multicomponent releases from source and dispersion experimentation/modeling, corresponding information is needed in the toxicology arena. Unfortunately, even toxic response data of humans to single component exposures are woefully inadequate for a large number of chemical species, and the assessment of the toxicology of chemical mixtures is an active area of research.
5. There are no toxicology testing protocols that exist for studying episodic releases on animals. This has been in general a neglected aspect of toxicology research. There are experimental problems associated with the testing of toxic chemicals at high concentrations for very short durations in establishing a concentration/time profile. In testing involving fatal concentration/time exposures, a further question exists of how to incorporate early and delayed fatalities into the study results.

9.7.1 Uncertainties Related to Toxicity Information

Toxicity information for many of the chemicals found at Superfund sites is often limited. Consequently, there are varying degrees of uncertainty associated with the toxicity values calculated for these chemicals. Sources of uncertainty associated with toxicity values may include the following:

1. Using dose–response information from effects observed at high doses to predict the adverse health effects that may occur following exposure to the low levels expected from human contact with the agent in the environment
2. Using dose–response information from short-term exposure studies to predict the effects of long-term exposures and vice versa
3. Using dose–response information from animal studies to predict effects in humans
4. Using dose–response information from homogeneous animal populations or healthy human populations to predict the effects likely to be observed in the general population consisting of individuals with a wide range of sensitivities

An understanding of the degree of uncertainty associated with toxicity values is an important part of interpreting and using these values. Therefore, as part of the toxicity assessments, a discussion of the strength of the evidence of the entire range of principal and supporting studies should be included. The degree of confidence ascribed to a toxicity value is a function of both the quality of the individual study from which it was derived and the completeness of the supporting database. The EPA-verified RfDs found in IRIS are accompanied by a statement of the confidence that the evaluators have in the RfD itself, the critical study, and the overall database. All EPA-verified slope factors are accompanied by a weight-of-evidence classification, which indicates the likelihood that the agent is a human carcinogen. The weight-of-evidence classification is based on the completeness of the evidence that the agent causes cancer in experimental animals and humans. These designations should be used as one basis for the discussion of uncertainty.

Initially, a safety factor was employed to account for uncertainty by identifying the dose at which a human would not be adversely affected. In addition, procedures have defined a safe level of exposure as a fraction of the dose level for which no adverse effects are observed; this level was defined earlier as the NOEL. Thus, the safety factor approach to obtain acceptable human exposure levels is based on the existence of a threshold dose level below which no adverse effects are observed. A *de minimis* approach (based on a risk that bypasses regulatory oversight and/or is deemed unimportant) helps identify suggested insignificant risks that do not deserve attention.

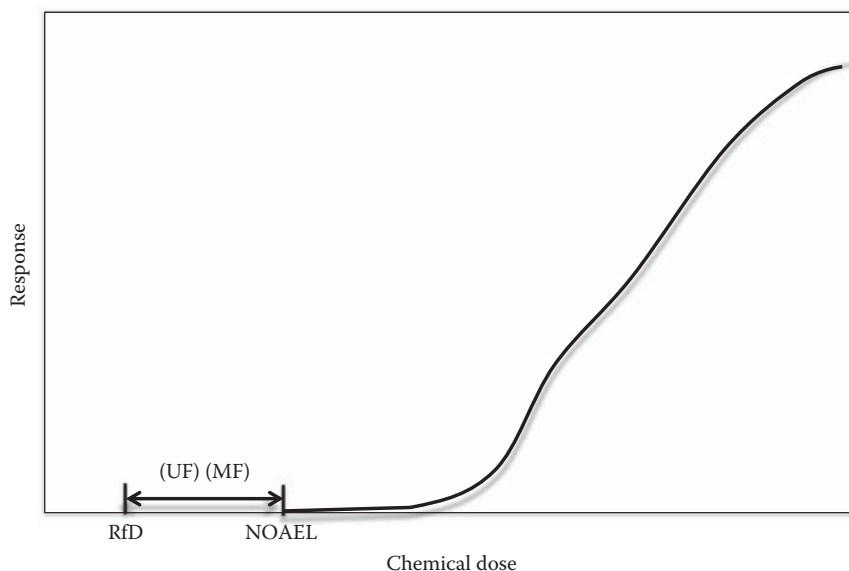


FIGURE 9.6
Scheme for establishing RfDs.

Illustrative Example 9.11

Describe the process of setting an RfD using a dose–response curve.

Solution

RfD is "... an estimate (with an uncertainty of one order of magnitude or more) of a lifetime dose which is likely to be, without significant risk to human populations." RfD is determined by dividing the NOAEL dose of a substance by the product of the UFs and MFs as is defined in Equation 9.10 and illustrated in Figure 9.6:

$$RfD = \frac{NOAEL}{UF \times MF} \quad (9.10)$$

where *UF* is the uncertainty factor that is generally in multiples of 10 to account for variation in the exposed population (to protect sensitive subpopulations), uncertainties in extrapolating from animals to humans, uncertainties in using subchronic instead of chronic study data, and uncertainties in using the LOAEL rather than the NOAEL, and *MF* is a modifying factor that ranges from 0 to 10 to reflect qualitative professional judgment of additional uncertainties in the data from available studies.

Illustrative Example 9.12

Define and compare the following pairs of parameters used in dose-response analysis:

1. NOEL and NOAEL
2. LOEL and LOAEL
3. ADI and RfD

Solution

1. NOEL is an acronym for “no observed effect level,” the highest dose of a toxic substance that will not cause an effect. NOAEL is an acronym for “no observed adverse effect level,” the highest dose of the toxic substance that will not cause an *adverse* effect.
2. LOEL is an acronym for “lowest observed effect level,” the lowest dose tested for which effects were shown. LOAEL is an acronym for “lowest observed adverse effect level,” the lowest dose tested for which *adverse* effects were shown. Both NOEL and LOEL are based on a wide range of toxic substance effects, while NOAEL and LOAEL are based on only adverse effects. Neither set of parameters takes into account the individual variation in susceptibility.
3. ADI, the acceptable daily intake, is the level of daily intake of a particular substance that will not produce an adverse effect. RfD, the reference dose, is an estimate of a daily exposure level for the human population that will not produce an adverse effect. The RfD development follows a stricter procedure than that used for the ADI. This sometimes results in a lower value for ADI.

Comment: When using data for LOELs, LOAELs, NOELs, or NOAELs, it is important to be aware of their limitations. As discussed in this chapter, statistical uncertainty exists in the determination of these parameters due to the limited number of animals used in the studies to determine these values. However, any toxic effect might be used for the NOAEL and LOAEL so long as it is the most sensitive toxic effect considered likely to occur in humans.

Illustrative Example 9.13

The drinking water maximum contaminant level (MCL) set by the EPA for atrazine is 0.003 mg/L and its RfD is 3.5 mg/kg-day. How many liters of water containing atrazine at its MCL would a person have to drink each day to exceed the RfD for this triazine herbicide?

Solution

Assuming that those exposed can be represented by a 70 kg individual, the volume of drinking water at the MCL to reach the RfD for atrazine is

$$\frac{(3.5\text{mg/kg-day})(70\text{kg})}{(0.003\text{mg/L})} = 81,667\text{L/day}$$

This large volume indicates that there is either no health problem or there is considerable uncertainty (i.e., the product of the UFs is large) in estimating an RfD for atrazine.

Illustrative Example 9.14

Due to contamination from a metal plating facility, the water from a nearby community water supply well was shown to contain cyanide at a concentration of $10\mu\text{g/L}$, nickel at $95\mu\text{g/L}$, and chromium(III) at $10,200\mu\text{g/L}$. If the daily water intake is assumed to be 2L, and the body weight of an adult is 70 kg, do these noncarcinogenic chemicals pose a health problem?

Solution

The dose, D , for cyanide is

$$D = \frac{(0.01\text{mg/L})(2\text{L/day})}{(70\text{kg})} = 2.86 \times 10^{-4}\text{mg/kg-day}$$

The remaining calculations are shown in Table 9.6. The chemical's RfD values were obtained from the IRIS database. The individual hazard index values as well as the cumulative HI are below 1.0 (unity) and this preliminary evaluation does not indicate an unacceptable hazard from this exposure.

Illustrative Example 9.15

Are the chances of getting cancer for someone who is exposed to a small amount of a toxic chemical once the same as for someone who is exposed to a small amount of that same toxic chemical everyday?

TABLE 9.6

Calculations for Illustrative Example 9.15

Substance	Concentration, C (mg/L)	Dose (mg/ kg-day)	RfD (mg/ kg-day)	Hazard Index (Dose/RfD)
Cyanide	0.010	5.71×10^{-4}	0.0006	0.476
Nickel	0.095	2.71×10^{-3}	0.02	0.136
Chromium (III)	10.2	2.91×10^{-1}	1.5	0.194
Total HI				0.806

Solution

Since this compound is stated to be a carcinogen, it is generally accepted that there would not be a threshold dose for the adverse affect it causes. For carcinogens, the risk is defined as the product of the slope factor times the dose, so the greater the dose, the greater the potential risk. The chances of cancer are never zero, but increase with increased exposure to carcinogens.

Illustrative Example 9.16

The air in a factory contains 500ppm_v of butane ($TLV=800\text{ppm}_v$), 100ppm_v of cyclohexane ($TLV=300\text{ppm}_v$), 100ppm_v of ethyl ether ($TLV=400\text{ppm}_v$), and 500ppm_v of liquid petroleum gas ($TLV=1000\text{ppm}_v$). Is this a safe work place?

When two or more chemical substances that act upon the same organ system are present, their combined effect, rather than the isolated individual effects, must be considered, and a modified form of Equation 9.2 is provided in Equation 9.11 to account for multiple chemical exposures. If the sum of the following fractions exceeds unity, the threshold limit of the mixture has been exceeded:

$$TLV(\text{mixture}) = \frac{C_1}{T_1} + \frac{C_2}{T_2} + \frac{C_3}{T_3} + \frac{C_4}{T_4} + \dots + \frac{C_n}{T_n} > 1; \quad (9.11)$$

Not a safe working place

$TLV(\text{mixture}) = 1$; Caution

$TLV(\text{mixture}) < 1$; A safe working place

where

C is the concentration measured in work area, ppm_v

T is the corresponding $TLVs$, ppm_v

Solution

Based on Equation 9.11, the mixture of butane, cyclohexane, ethyl ether, and liquid petroleum gas is evaluated in terms of the combined TLV as follows:

Butane + cyclohexane + ethyl ether + liquid petroleum gas

$$\begin{aligned} TLV(\text{mixture}) &= \frac{500\text{ppm}_v}{800\text{ppm}_v} + \frac{100\text{ppm}_v}{300\text{ppm}_v} + \frac{100\text{ppm}_v}{400\text{ppm}_v} \\ &+ \frac{500\text{ppm}_v}{1000\text{ppm}_v} = 1.708 > 1 \end{aligned}$$

Therefore, this room is not a safe working place and air concentrations of these compounds should be controlled to prevent life- and

health-threatening situations at this facility. For TLVs of other chemicals, refer to the *American Conference of Industrial Hygienist Handbook* [14].

Illustrative Example 9.17

Workers in a certain plant are exposed for 8 h periods simultaneously to acetone (300 ppm_v), *sec*-butyl acetate (100 ppm_v), and methyl ethyl ketone (150 ppm_v). The TLV standard for acetone is 750 ppm_v, for *sec*-butyl acetate is 200 ppm_v, and for methyl ethyl ketone is 200 ppm_v. Note that these 1989 TLVs are the maximum exposures permitted for a person for a 40 h week. Is the atmosphere to which the workers are exposed in excess of the standards?

Solution

Exposure to a mixture of three substances exceeds the TLV standard when Equation 9.11 holds, i.e.,

$$TLV(\text{mixture}) = \left(\frac{C_1}{T_1} \right) + \left(\frac{C_2}{T_2} \right) + \left(\frac{C_3}{T_3} \right) > 1$$

In the case described in the problem statement,

$$\left(\frac{300 \text{ ppm}_v}{750 \text{ ppm}_v} \right) + \left(\frac{100 \text{ ppm}_v}{200 \text{ ppm}_v} \right) + \left(\frac{150 \text{ ppm}_v}{200 \text{ ppm}_v} \right) = 1.65 > 1$$

Therefore, the exposure is greater than the acceptable TLV. Note that this method of estimating combined exposure is valid only when the various substances all have somewhat similar toxic effects.

Exceptions to the aforementioned equation may be made when there is good reason to believe that the primary effects of the different chemicals are not in fact additive but *independent*, e.g., when purely local effects on different organs of the body are produced by the various components of the mixture. In such cases, the threshold limit ordinarily is exceeded only when at least one term in Equation 9.11 has a value exceeding unity.

Illustrative Example 9.18

What is the maximum number of excess lifetime cancer cases expected for a population of 5000 adults with a daily intake of 0.20 mg of benzene? The slope factor for benzene may be assumed to be 0.029 (mg/kg-day)⁻¹.

Solution

Assume an adult body weight of 70 kg. The lifetime cancer risk is calculated as

$$\text{Individual cancer risk} = \frac{(0.20 \text{ mg/day})(0.029 \text{ kg-d/mg})}{(70 \text{ kg})}$$

$$= 8.29 \times 10^{-5} (\text{fractional basis}) = 8.29 \times 10^{-3} \%$$

$$\text{Maximum cancer cases} = (\text{Individual risk})(\text{Exposed population})$$

$$= (8.29 \times 10^{-5})(5000) = 0.41 \text{ lifetime cancer cases}$$

Fractional numbers can pose a problem but should be rounded to the next integer. Therefore, this would represent a maximum of one additional lifetime cancer case in the exposed population of 5000 individuals.

Illustrative Example 9.19

Two large bottles of flammable solvent were ignited by an undetermined ignition source after being knocked over and broken by a janitor while cleaning a 10 ft \times 10 ft \times 10 ft research laboratory. The laboratory ventilator was shut off and the fire was fought with a 10 lb CO₂ fire extinguisher. As the burning solvent had covered much of the floor area, the fire extinguisher was completely emptied in putting out the fire.

The immediately dangerous to life and health (IDLH) level for CO₂, set by the National Institute for Occupational Safety and Health (NIOSH), is 50,000 ppm_v. At that level, vomiting, dizziness, disorientation, and breathing difficulties occur after a 30 min exposure; at a 100,000 ppm_v, death can occur after a few minutes, even if the oxygen in the atmosphere would otherwise support life.

Calculate the concentration of CO₂ in the room after the fire extinguisher is emptied. Does it exceed the IDLH value? Assume that the gas mixture in the room is uniformly mixed, that the temperature in the room is 30°C (warmed by the fire above normal room temperature of 20°C) and that the ambient pressure is 1 atm.

Solution

First calculate the number of moles of CO₂ discharged by the fire extinguisher:

$$\text{Moles of CO}_2 = \frac{(10 \text{ lb CO}_2)(454 \text{ g/lb})}{(44 \text{ g/gmol CO}_2)} = 103 \text{ gmol CO}_2$$

Calculate the volume of the room:

$$\text{Room volume} = (10 \text{ ft})(10 \text{ ft})(10 \text{ ft})(0.0283 \text{ m}^3 / \text{ft}^3) = 28.3 \text{ m}^3 = 28,300 \text{ L}$$

Next, calculate the total number of moles of gas in the room by applying the ideal gas law:

$$\text{Moles of gas} = \frac{PV}{RT} = \frac{(1\text{atm})(28,300\text{L})}{(0.08206\text{atm}\cdot\text{L}/\text{gmol}\cdot\text{K})(303\text{K})} = 1138\text{gmol of gas}$$

Calculate the concentration, or mole fraction, of CO₂ in the room:

$$\text{Mole fraction} = \frac{\text{gmol CO}_2}{\text{gmol gas}} = \frac{103\text{gmol CO}_2}{1138\text{gmol gas}} = 0.0905$$

Convert this fraction to a percent and compare to the IDLH and lethal levels:

$$\% \text{ CO}_2 = (\text{Mole fraction})(100) = (0.0905)(100) = 9.05$$

The IDLH level is 5.0% and the lethal level is 10.0%. Therefore, the level in the room of 9.05% does exceed the IDLH level for CO₂. It is also dangerously close to the lethal level. The person extinguishing the fire is in great danger and should take appropriate safety measures immediately.

Illustrative Example 9.20

The dynamic seal for a control valve suddenly starts leaking toluene-2,4-diisocyanate (TDI) vapor at a rate of 40 cm³/h into a 12 ft × 12 ft × 8 ft room. The air in the room is uniformly mixed by a ceiling fan. The background TDI vapor concentration is 1.0 ppb_v. Air temperature and pressure are 77°F and 1 atm, respectively. Calculate the ppm_v value of leaking TDI vapor if its vapor pressure is 35 mmHg at 25°C. Also, calculate the number of minutes after the leak starts that a person sleeping on the job would be at risk of being exposed to TDI vapor with respect to the STEL, 1/4 LEL (lower explosive limit), and TLV-TWA.

TDI exposure limit values are as follows:

1. Short-term exposure limit (STEL) = 0.02 ppm_v
2. 25% of 1/4 LEL = 1/4 (0.9%) = 0.00225 v/v
3. TLV-TWA = 0.005 ppm_v

Solution

1. Calculate the maximum TDI vapor concentration in ppm_v based on its vapor pressure at the leak:

$$\begin{aligned} \text{Maximum vapor concentration} \\ &= (35\text{mmHg}/760\text{mmHg/atm})(1,000,000\text{ppm}_v/\text{atm}) \\ &= 46,100\text{ppm}_v \end{aligned}$$

The reader is left to consider why this is a maximum concentration since the TDI leak is uncontrolled. HINT: Consider what happens when the partial pressure “exceeds” the vapor pressure of a gas.

- Calculate the TDI vapor concentration (ppm_v) in the room as a function of time, t (min):

$$C(\text{ppm}_v) = 0.001 \text{ ppm}_v + \frac{(40 \text{ cm}^3/\text{h})(1 \text{ h}/60 \text{ min})(1 \text{ L}/1,000 \text{ cm}^3)(t \text{ min})}{(12 \text{ ft})(12 \text{ ft})(8 \text{ ft})(0.02823 \text{ m}^3/\text{ft}^3)(1,000 \text{ L}/\text{m}^3)} \times \left(\frac{1,000,000 \text{ ppm}_v}{v/v} \right)$$

$$C(\text{ppm}_v) = 0.001 \text{ ppm}_v + 2.04 \times 10^{-2} t \text{ ppm}_v$$

where t is the time in minutes measured from the time the leak starts.

- Express the average concentration in terms of time:

$$C_{avg} = \frac{[0.001 + (0.001 + 2.04 \times 10^{-2} t)]}{2}$$

- Calculate the time, t , in minutes to reach the STEL of 0.02 ppm_v using the aforementioned equation for $C_{avg} = 0.02 \text{ ppm}_v$:

$$C_{avg} = 0.02 = \frac{[0.001 + (0.001 + 2.04 \times 10^{-2} t)]}{2}$$

$$0.04 = (0.002 + 2.04 \times 10^{-2} t)$$

$$t = \frac{0.038}{(2.04 \times 10^{-2})} = 1.86 \text{ min}$$

It should be noted that this is much shorter than the averaging time for the STEL exposure limit of 15 min. Using a 15 min averaging period, the average concentration in the room is

$$C_{avg} = \frac{[0.001 + (0.001 + 2.04 \times 10^{-2} (15))]}{2} = \frac{(0.002 + 0.306)}{2} = 0.154 \text{ ppm}_v$$

which is nearly eight times higher than the STEL

- Calculate the time in minutes, t , to reach 1/4 the LEL = $0.00225 v/v = 2,250 \text{ ppm}_v$:

$$2250 \text{ ppm}_v = 0.001 + 2.04 \times 10^{-2} t$$

$$t = \frac{(2250 - 0.001)}{2.04 \times 10^{-2}} = 110,300 \text{ min}$$

6. Calculate the average concentration after the TWA averaging time of 8 h is reached:

For an 8 h averaging period, $t = 8 \text{ h} = 480 \text{ min}$, the mean TDI concentration from the expression in part (3) is

$$C_{avg} = \frac{[0.001 + (0.001 + 2.04 \times 10^{-2}(480))]}{2} = 4.897 = 4.9 \text{ ppm}_v$$

Therefore, the mean TDI vapor concentration in the room over the 8 h averaging period exceeds the TLV by a factor of 980. It should be noted that this 8 h averaged concentration is nearly twice the IDLH value of 2.5 ppm_v , so a serious problem obviously exists with this release!

Illustrative Example 9.21

List some human responses to dust exposure.

Solution

1. Immunologically induced airway constriction (asthma)
2. Pharmacologically induced airway constriction
3. Irritant gases or fumes producing reflective constriction.
4. After prolonged exposure, dusts may cause industrial bronchitis

Dust exposure receives treatment in Chapter 13.

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10

Exposure Assessment

10.1 Introduction

As noted, one critical component of environmental health risk assessment (HRA) is exposure assessment. It is defined as the determination of the concentration of chemicals in time and space at the location of receptors and/or target populations. This description must therefore also include an identification of all major pathways for movement and transformation of a toxic material from a source to receptors. Ideally, concentrations should be identified as a function of time and location, and should include all major transformation processes. The principal pathways generally considered in exposure assessments are atmospheric transport and surface/groundwater transport. Since atmospheric dispersion has received the bulk of the treatment in the literature, a good part of the material to follow will address this topic.

The exposure assessment process consists of two basic methods for determining the concentration of a chemical to which receptor target populations are exposed:

1. The first is the direct measurement of the intensity, frequency, and duration of human or animal exposure to a pollutant currently present in the environment. This is a common practice in occupational settings. In some situations, however, either concentrations are too low to be detected against background, or direct measurement is too costly or difficult to implement.
2. Under these circumstances, the second method is employed. It involves the use of mathematical models to estimate hypothetical exposures that might arise from the release of new chemicals into the environment. This chapter discusses some of these models.

In its most complete form, an exposure assessment should describe the magnitude, duration, timing, and route of exposure of the hazardous agent, along with the size, nature, and classes of the human, animal, aquatic, or wildlife populations exposed, and the uncertainties in all estimates. The exposure

assessment can often be used to identify feasible prospective control options and to predict the effects of available treatment technologies for controlling or limiting exposure [1]. However, the estimation of the likelihood of exposure to a chemical remains a different task. More attention has been recently focused on exposure assessment because many of the risk assessments performed in the past used too many overly conservative assumptions. This, in turn, resulted in an overestimation of the actual exposure risk posed to vulnerable receptors.

Obviously, without exposure(s) there are no risks. To experience adverse effects, one must first come into contact with the toxic agent(s). Exposures to chemicals can occur via inhalation of air (breathing), intake into the body via ingestion of water and food (eating and drinking), or adsorption through the skin. These intake processes are followed by chemical distribution through the body via the bloodstream. After being absorbed and distributed, the chemical(s) may be metabolized and excreted, either as the parent compound or as their metabolites and/or their conjugate adducts. The principal excretory organs are the kidney, liver, and lungs.

As noted earlier, the main pathways of exposure considered in human exposure assessments are via atmospheric, surface, and groundwater transport. However, the ingestion of toxic materials that have passed through the aquatic and terrestrial food chains, and dermal absorption, are two other pathways of potentially significant human exposure. The physical and chemical properties of the chemical under study will dictate the primary route(s) by which exposure will occur. Naturally, the chemical under study should be analyzed for the primary route(s) of human exposure. There are instances where humans may be exposed to a compound by more than one route, i.e., by inhalation and oral ingestion. Which is the most significant route of administration? Assuming approximately equal exposure by both routes, it is recommended that the chemical exposure assessment should focus on the route posing the greater risk. For those situations where one route of exposure predominates over another, the predominate route should be considered. Once an exposure assessment determines the quantity of a chemical with which human populations may come in contact, the information can be combined with toxicity data (from dose-response information, see Chapter 9) to estimate potential health risks [2].

This chapter focuses on some of the practical considerations of exposure assessment, with particular emphasis on atmospheric dispersion. Following this section, the reader is introduced to the Occupational Safety and Health Administration's (OSHA) "Components of an Exposure Assessment Program." The next two sections deal with the development of the governing equations for dispersion in water systems and soils. Since the bulk of the work in this area is concerned with exposure to air pollutants, the remainder of the chapter focuses on atmospheric dispersion applications.

The effective height of an emission is next considered in view of the various equations and correlations currently in use. Atmospheric dispersion equations for continuous sources are reviewed; the effects of multiple sources as well as emissions (including particulates) from line and area sources are also briefly discussed. Both continuous and instantaneous releases are of concern in accident and emergency management. Although the bulk of the material here has been presented for continuous emissions for a point source (e.g., a stack), the chapter also includes discussion of what has been referred to in the literature as a “puff” model, namely, an equation that can be used for estimating the effect of discharges from instantaneous (as opposed to continuous) sources. The chapter concludes with a short section on available computer models.

The reader should once again note that two general types of potential health risk from chemical exposures exist. These are classified as follows:

1. *Chronic*. Risk related to continuous exposures over long periods of time, generally several months to years. Concentrations of emitted chemicals are usually relatively low. This subject area falls in the general domain of HRA, and it is this subject that is addressed in this and the next chapter. Thus, in contrast to the acute (short-term) exposures that predominate in hazard risk assessments (HZRAs), chronic (long-term) exposures are the major concern in HRAs.
2. *Acute*. Risk related to exposures that occur for relatively short periods of time, generally from minutes to 1 to 2 days. Concentrations of emitted chemicals are usually high relative to their no-effects levels. In addition to inhalation, airborne substances might directly contact the skin, or liquids and sludges may be splashed on the skin or into the eyes, leading to adverse health effects in acute risk settings. This subject area falls, in a general sense, in the domain of HZRA and is addressed in Part III.

Before proceeding to the main chapter contents, the reader should note that the exposure effect, E , can be described in equation form. If C and Δt represent the chemical concentration, mg/m^3 , and time of exposure, d , respectively, one may write an expression for the resultant effects as

$$E = (C)(\Delta t) \quad (10.1)$$

In addition, the dose of a chemical that occurs via an inhalation pathway, I , may be expressed as

$$I = \frac{(C)(IR)(AF)}{BW} \quad (10.2)$$

where

IR is the inhalation rate, m^3/day

AF is the absorption (intake) factor, dimensionless

BW is the receptor body weight, kg ; typical metric units of I are $\text{mg}/\text{kg}\cdot\text{day}$

Illustrative Example 10.1

Describe the actions that can occur during and following the absorption of a chemical agent by the skin.

Solution

Four possible actions that can occur include

1. Skin, films of sweat, or fat layers under the skin may act as a barrier to agent penetration.
2. The agent may react with the skin to cause primary irritation.
3. The agent may penetrate the skin and cause sensitization reactions.
4. The agent may penetrate the skin, enter the bloodstream, and act as a "poison."

The routes through the skin include

1. Epidermal cells—usually the main pathway through the skin
2. Sweat glands
3. Other glands
4. Hair follicles

Illustrative Example 10.2

Describe uncertainties as they relate to exposure models.

Solution

Uncertainty is a term that is addressed repeatedly in this book. This chapter is no exception. Uncertainties exist in exposure models because they are mathematical approximations of real system behavior. These uncertainties arise from two sources:

1. Imprecision in the model description of physical and chemical processes
2. Uncertainties in model input parameters

The best method of determining model uncertainty is via a comparison of the model's predictions with either field or laboratory observations, or both, made over the range of conditions for which application of model was intended.

10.2 Components of an Exposure Assessment

Exposure is defined as the contact of a chemical or physical agent with the outer boundary of an organism (humans in the case of HRA) [3]. The magnitude of exposure is determined by measuring or estimating the amount of an agent available at the body's exchange boundaries (i.e., the lungs, stomach, and skin) during a specified time period. Exposure assessment is the determination or estimation (qualitative or quantitative) of the magnitude, frequency, duration, and route of exposure. Exposure assessments may consider past, present, and future exposures, using varying assessment techniques for each phase. Estimates of current exposures can be based on measurements or models of existing conditions; those of future exposures can be based on models of future conditions; and, those of past exposures can be based on measured or modeled past concentrations or measured chemical concentrations in tissues.

The exposure assessment process is carried out through the following four steps.

10.2.1 Step 1: Characterization of Exposure Setting

In this step, the exposure assessor characterizes the exposure setting with respect to the general physical characteristics of the site of the release and the characterizations of the populations on and near the site. Basic site characteristics such as climate (temperature, wind speed, wind direction, lower atmospheric stability, and rainfall), vegetation, groundwater hydrology, and the presence and location of surface waters are identified in this step. Populations are also identified and are described with respect to those characteristics that influence exposure, such as location relative to the site, activity patterns, and the presence of sensitive subpopulations. This step considers the characteristics of the current population, as well as those of any potential future populations that may differ under an alternate land use scenario.

Sources of this information include site descriptions and data from the preliminary assessment (PA), site inspection (SI), and any remedial investigation (RI) reports that might be available. Other sources include local soil surveys, wetland maps, aerial photographs, and reports by the National Oceanographic and Atmospheric Administration (NOAA) and the U.S. Geological Survey (USGS). One can also consult with appropriate technical experts (e.g., hydrogeologists and air modelers) as needed to characterize the site.

10.2.2 Step 2: Identification of Exposure Pathways

In this step, the exposure assessor identifies those pathways by which the previously identified populations may be exposed to chemical releases from

the site under study. Each exposure pathway describes a unique mechanism by which a chemical may be transported and transformed as it travels to a population that may be exposed to the chemical at or originating from the site. After a chemical is released to the environment, these exposure pathways may involve one or more of the following processes:

1. Transport (e.g., convected downstream in water or on suspended sediment or through the atmosphere)
2. Physical transformation (volatilization, precipitation, etc.)
3. Chemical transformation (photolysis, hydrolysis, oxidation, reduction, etc.)
4. Biological transformation (biodegradation, transformation, mineralization, etc.)
5. Accumulation in one or more media (including the receptor)

Exposure pathways are identified based on consideration of the sources, release scenarios, types, and location of chemicals at the site, the likely environmental fate (including persistence, partitioning, transport, and intermedia transfer) of these chemicals, and the location and activities of the potentially exposed populations. Exposure points (points of potential contact with the chemical) and routes of exposure (e.g., ingestion and inhalation) are identified for each exposure pathway.

All available site descriptions and data from the PA, SI, and RI reports should be engaged to determine possible release sources for a site. One should attempt to identify potential release mechanisms and corresponding chemical transfer media for past, current, and future releases. Monitoring data, in conjunction with information on source locations to support the analysis of past, continuing, or threatened releases, should be employed. For example, soil contamination near an old tank would suggest the tank or transfer piping (source) ruptured or leaked (release mechanism) to the ground (receiving media). Any source that could be an exposure point in addition to a release source (e.g., open barrels or tanks, surface waste piles or lagoons, and contaminated soil) should also be noted.

10.2.3 Step 3: Quantification of Exposure

In this step, the exposure assessor quantifies the magnitude, frequency, and duration of exposure for each pathway identified in Step 2. This step is most often conducted in two stages: estimation of exposure concentrations and calculation of intakes. The later estimation is considered in Step 4. In this part of Step 3, the exposure assessor determines the concentration of chemicals that the receptors will be exposed to over the exposure period. Exposure concentrations are estimated using monitoring data and/or chemical transport and environmental fate models relevant for a given exposure pathway. Modeling

may be used to estimate future chemical concentrations in media that are currently contaminated or that may become contaminated, and current concentrations in media and/or at locations for which there are no monitoring data. The bulk of the material in this chapter is concerned with this step.

10.2.4 Step 4: Quantification of Intakes

In this step, the exposure assessor calculates chemical-specific exposures for each exposure pathway identified in step 2, generally normalized to receptor body weight. Exposure estimates are expressed in terms of the mass of substance in contact with the body per unit body weight per unit time (e.g., mg chemical/kg body weight/day, also expressed as mg/kg-day). These exposure estimates are termed “intakes” (for the purposes of this chapter) and represent a normalized exposure rate. Several terms that are equivalent or related to intake commonly found in EPA documents and other literature include:

1. Normalized exposure rate (intake)
2. Administered dose (intake)
3. Applied dose (intake)
4. Absorbed dose (intake \times absorption factor)

Chemical intakes are calculated using equations that include variables for exposure concentration, contact rate, exposure frequency, exposure duration, body weight, and exposure averaging time. The values of some of these variables depend on site conditions and the characteristics of the potentially exposed population.

After intakes have been estimated, they are organized by population as appropriate. Then, the sources of uncertainty (e.g., variability in analytical data, modeling results, parameter assumptions) and their effect on the exposure estimates are evaluated and summarized. This information on uncertainty is important to site decision makers who must evaluate the results of the exposure and risk assessment and make decisions regarding the degree of risk reduction required at a site. The exposure assessment concludes with a summary of the estimated intakes for each pathway evaluated.

In summary, a preliminary description of the exposure scenario should be obtained, which answers the following questions:

1. Where, when, and how will the release of the toxicant occur?
2. What is in the immediate vicinity of the release?
3. What is the quantity, physical state, and chemical identity of the released material?
4. What are the concentrations and durations of exposure in the area of the toxicant's release?

5. Will the toxicant be distributed to a larger area, and if so what will be its form (physical and chemical), concentration, and duration of existence throughout the area of distribution? This description should include the concentrations at various locations and times throughout its existence, and it should include air and waterborne materials as well as those taken up by biological materials such as plants and animals.

To estimate exposure, the EPA has relied on a standard assumption, called the maximally exposed individual (MEI). However, the EPA has acknowledged that the MEI standard considerably overestimates individual exposure. As a more realistic alternative, the Electric Power Research Institute (EPRI) developed the reasonably exposed individual (REI) measure of exposure. In both cases, the exposed individual lives in an area with the highest concentration of plant emissions. The MEI measure assumes that the individual is sedentary, breathes at a steady rate, and lives outside any structure for his or her entire lifetime. The REI measure accounts for time spent indoors (where exposure to some pollutants is reduced) and time spent working in distant areas, residential relocations, and physical activity (and hence varying breathing rates), and for the EPRI-specific cases dealing with power plant emissions, including the replacement of fossil-fuel generation units after a half century or more of operation.

10.3 Dispersion in Water Systems

Enormous amounts of waste discharged into water systems are degrading water quality and causing increased human health problems. In assessing this pollution, there are two distinct problem areas. The first, and worst, is in marine estuaries and associated coastal waters. As fewer and fewer alternatives remain for land disposal, wastes are finding their way more often into water. The second problem area consists of the oceans themselves, although it is believed that not much of a problem currently exists there because relatively little waste is dumped directly into the oceans. Municipal sewage and agricultural runoff are major sources of water pollution; yet in the aggregate, industrial discharges represent the largest source of toxic pollutants entering the marine environment. The major reason for this is that marine disposal, if available, is much cheaper for industry than other ways of disposing of their wastes.

In addition to the normal, everyday pollutant emissions into water systems is the ever-present threat of a discharge resulting from an accident, an emergency, or a combination of these. This subject receives treatment in Part III. The dispersion and ultimate fate of such pollutants is a major concern to

environmental engineers and scientists. It is for this reason that the present section on dispersion applications in water systems has been included. Much of this material has been “excerpted” and edited from one of the classic works in this field by Thomann and Mueller [4].

In general, the role of the water quality engineer and the scientist is to analyze water quality problems by dividing each case into its principal components. These are:

1. *Inputs*: the discharge into the environment of residue from human and natural activities
2. *Reactions and physical transport*: the chemical and biological transformations and water movement that result in different levels of water quality at different locations in time in an aquatic ecosystem
3. *Output*: the resulting concentration of a substance, such as dissolved oxygen (DO) or nutrients, at a particular location in a river or stream and during a particular time of the day or year

Calculations are generally estimated using simple, one-directional, steady-state approaches. Models to simulate the migration of chemicals over a land surface toward a receiving body of water (watershed modeling) remain limited.

These chemical inputs are discharged into rivers, lakes, estuaries, groundwater, or oceanic regions. After the occurrence of chemical, biological, and physical processes (e.g., biodegradation, chemical hydrolysis, and physical sedimentation), these inputs result in a specific concentration of a substance in a given water body. Concurrently, through various mechanisms of public hearings, legislation, and evaluation, a desirable beneficial use has been established for the particular water body under study. Such a desirable beneficial use is translated into public health and/or ecological criteria, which are then compared to the concentration of the substance resulting from the waste discharge. This comparison may demonstrate the need for an environmental control program if the actual or forecasted concentration is not equal to or less than the concentration that is required to protect the designated use for the water body. Environmental controls are then instituted to ensure the reduction necessary to reach the required concentration. The same basic philosophy is applied in treating accidental and/or emergency and/or catastrophic discharges (see Part III) into water systems.

Wastewater discharges can be divided into two broad categories: point sources and nonpoint sources. Point source inputs are generally continuous sources and are considered to have a well-defined point of discharge, which under most circumstances is a pipe or group of pipes that can be located and associated with a particular discharger. The two principal point source categories are municipal wastewater treatment plant effluents and industrial discharges.

The principal nonpoint sources are agricultural, silvicultural, atmospheric, and urban–suburban runoff. In each case, the distinguishing feature of the nonpoint source is that the origin of the discharge is diffuse, that is, it is not possible to relate the discharge to a specific, well-defined discharge origin or specific discharger. Furthermore, nonpoint sources may enter a given river or lake via overland flow, as in the case of agriculture, or directly to the surface of the water as an atmospheric input. Urban and suburban runoff may enter the water body through a large number of smaller drainage pipes designed to carry not wastes but stormwater runoff. In some instances, stormwater discharge may enter a surface water body primarily via a large pipe draining a similarly large runoff area. Other nonpoint sources include pollution due to drainage from abandoned mines and from construction activities, as well as leaching from land disposal of solid and/or hazardous waste.

10.3.1 Rivers and Estuaries

The best physical model that can be used to describe a stream or river is a tubular flow reactor [5]. The governing equations then become 1-D in the Cartesian (rectangular) coordinate system in the direction of the moving water. Most streams and rivers are subjected to sources or sinks of a pollutant, which are distributed along the length of the stream. An example of an external source is runoff from agricultural areas, whereas oxygen-demanding material distributed over the bottom of the stream exemplifies an in-stream or internal source. The concentration of a pollutant in a stream or river due to multiple point and/or distributed sources can be represented by the linear summation of the responses due to the individual sources plus the response due to any upstream boundary condition. Solutions are available for streams with multiple sources in which flows and velocities vary but are constant for a given length, although this situation is sometimes treated analytically as a 1-D transport equation expressed in spherical coordinates [4,5].

The region between the free-flowing river and the ocean is a fascinating diverse and complex water system: the coastal regime of estuaries, bays, and harbors. The ebb and flow of the tides, the incursion of salinity from the ocean, and the influx of nutrients from the upstream drainage all contribute to the generation of a unique aquatic ecosystem. Estuarine and wetland regions are considered to be crucial to the maintenance of major fish stocks such as the striped bass and the bluefish, which to varying degrees use the estuarine areas as spawning and rearing grounds for their young. Many major cities are located along estuaries, primarily as a result of the historical need for ready access to national and international commerce routes. Such cities discharged large quantities of waste for many years, but because of the large volumes and continuous flushing of these estuaries, effects were not immediately felt. Later, however, especially in the 1950s, the load on these estuaries became very large, their water quality deteriorated rapidly, and

great interest centered on the analysis of water quality impacts and improvements necessary in these critical water bodies.

The movement of the tides into and out of estuaries and the associated density effects created by the incursion of salinity are of particular importance in describing the quality of such bodies of water. Tides are the movement of water above and below a datum plane, usual mean sea level. Tidal currents are the associated horizontal movement of the water into and out of an estuary. Tides and tidal currents are due to the attractive force of the moon and sun on the waters of the earth. There is a "pulling and tugging," which raises the water at certain locations and lowers it at others. These motions occur on a more or less cyclical basis, reflecting the regularity of the lunar and solar cycles. Tides are also present in lakes and seas, produced principally by winds blowing across the lake surface and "piling up" the water that, in turn, sets the lake into an oscillatory motion or *seiche*. The approximately regular motion of the lake results in a motion in lake tributaries similar to estuarine tides.

The interesting behavior of tidal currents in open offshore waters is due to the lack of physical boundaries. A tidal current tends to move about a point in a rotary-type current. Therefore, this type of current will tend to move any wastes discharged offshore in an elliptical pattern on which a net current drift may be superimposed.

An important characteristic of estuarine hydrology is the net flow through the estuary over a tidal cycle or a given number of cycles. This is the flow that, over a period of several days or weeks, flushes material out of the estuary; it is a significant parameter in the estimation of the distribution of estuarine water quality. If the estuary is well mixed from top to bottom and side to side (i.e., no significant gradients in velocity), the net flow at any location in the estuary is approximately equal to the sum of the upstream external flow inputs to the estuary. This is true because it is known that the flow inputs are not causing the estuary to overflow. Therefore, this flow must, on balance, be leaving the estuary at any cross section [4].

If the mixing is "perfect," the estuary behavior may be approximated by what chemical engineers define as a *continuous stirred tank reactor* (CSTR) [5]. However, accurately estimating the time and spatial behavior of water quality in estuaries is complicated by the effects of tidal motion as just described. The upstream and downstream currents produce substantial variations of water quality at certain points in the estuary, and the calculation of such variations is indeed a complicated problem. However, the following simplifications provide some remarkably useful results in estimating the distribution of estuarine water quality. To simplify this complicated system, the following assumptions can be applied:

1. The estuary is 1-D.
2. Water quality is described as a type of average condition over a number of tidal cycles.

3. The cross-sectional area and flow do not vary with downstream distance.
4. Steady-state conditions prevail.
5. Chemical reaction effects can be treated as first order [5].

A water body is considered to be a 1-D estuary when it is subjected to tidal reversals (i.e., reversals in direction of the water quality parameter are dominant). Since the describing (differential) equations for the distribution of either reactive or conservative (nonreactive) pollutants are linear, second-order equations, the principle of superposition discussed previously also applies to estuaries. The principal additional parameter introduced in the governing equation is a tidal dispersion coefficient. Methods for estimating this tidal coefficient are provided by Thomann and Mueller [4].

10.3.2 Lakes and Impoundments

It is often useful to describe lakes and reservoirs under the assumption that the body of water is completely mixed horizontally and vertically. This “completely mixed” assumption, which is similar to the one sometimes made in the cases of rivers and estuaries, is justified on the basis of wind mixing and internal density variations. An assumption of this type should be recognized as a gross approximation of the actual conditions within a lake, since variations in concentration of many substances will exist throughout the lake. However, the assumption permits many useful estimates to be made on the behavior of such systems. For this condition, the lake may be physically described as a perfectly mixed, stirred reactor. If overall flows are small and/or can be neglected, the system reduces to a batch reactor [5]. If the overall flows need to be considered, the governing equations may be made to take the form of the aforementioned continuously stirred tank reactor under either steady or transient conditions [5].

Treating a body of water as a completely mixed system can be a valuable approach for estimating the effects of human activities. It can be applied to a number of pollutants, including suspended and dissolved substances, as well as to heat balance computations. The vertical behavior of lakes is of particular importance because surface and bottom waters often exhibit quite different quality during periods of stratification. The estimation of vertical mixing is therefore of importance and, for some situations, a simple method can be used based on the completely mixed analysis.

The most important single factor in the evaporative loss of water is the incoming solar radiation. The vapor pressure (i.e., the maximum gaseous pressure of water vapor at a given temperature and 100% humidity) is also a primary variable and depends on the water temperature. Wind, air temperature, and water quality also contribute to the evaporative flux. When lakes are not well mixed, thermal gradients develop along the shore as well

as with depth. Many lakes, during summer heating, develop a warmer layer of water at the surface overlying a colder, deeper layer of water. The vertical temperature profile at the end of winter is often homogeneous from top to bottom. As spring warming begins, the surface layer begins to heat and, because of its lower density, begins to stratify and become a distinct layer from the deeper layer beneath it. By midsummer, a strong stratification may have formed and often three distinct vertical regions can be identified. During the fall, as surface temperatures begin to cool, the thermocline penetrates deeper into the lake. As winter approaches and vertical temperature gradients shift, very cold, more dense surface water will move downward through warmer, less dense water, causing the lake to “turnover” and fully mix vertically from top to bottom. Isothermal conditions then prevail again during winter through early spring. Another spring “turnover” may be observed in some lakes as surface ice melts and surface water layers reach a maximum density at 4°C and once again penetrate less dense, colder water below.

The major reasons for the behavior of vertical temperature gradients and density-driven mixing conditions that develop in water bodies are the low water thermal conductivity, and the rapid absorption and loss of heat in the first few meters of these lakes and impoundments. As the surface waters begin to heat or cool, heat transfer to and from lower layers is not as rapid and stratification or density-driven mixing conditions develop. The prediction of thermal behavior in lakes and reservoirs is an important power plant siting consideration and a major factor in preventing excessive thermal effects on sensitive ecosystems. Furthermore, the extent of thermal stratification influences the vertical dissolved oxygen (DO) profiles where reduced DO in the lower levels of reservoirs or impoundments often results from minimal exchange of this deeper water with shallower aerated water [4]. The reader is referred to Thomann and Mueller [4] for further discussion of the effect and quantification of the vertical mixing phenomena.

10.3.3 Groundwater

Depending on their density, chemicals or chemical mixtures that are highly immiscible in water and that are released to the ground in concentrated form will tend either to float as a light nonaqueous phase liquid (LNAPL) at the groundwater table surface or to penetrate the groundwater table as a dense nonaqueous phase liquid (DNAPL) and continue to move through the soil horizon until they reach a low-permeability confining layer somewhere below the water table surface. These LNAPLs and DNAPLs represent the source of hazardous pollutants that then slowly dissolve into the moving groundwater, producing dissolved plumes of contaminated groundwater that sometimes move miles away from their original sources of release. Leaking underground storage tanks containing fuels or oils are

the primary source of LNAPL groundwater problems, while used chlorinated solvents are the most important sources of groundwater DNAPL contamination.

The modeling of a groundwater chemical pollution problem may be 1-D, 2-D, or 3-D in scope. The proper approach is dependent on the problem context, i.e., the site conceptual model governing the problem. For example, the vertical migration of a chemical from a surface source to the water table is generally treated as a 1-D problem. Within an aquifer, this type of analysis may be valid if the chemical rapidly penetrates the aquifer so that concentrations are uniform vertically and laterally. This is likely to be the case when the vertical and lateral dimensions of the aquifer are small relative to the longitudinal scale of the problem or when the release essentially forms a point source at the water table surface.

More commonly, however, groundwater pollution problems are modeled using 2-D analysis. A typical groundwater plume has areal dimensions that are much larger than its vertical dimension. Therefore, chemicals dissolved in groundwater tend to achieve vertical uniformity a short distance from the source area, while the plume will advect in the longitudinal direction and disperse in both the lateral and longitudinal directions over time.

A 3-D analysis is generally used when a significant vertical concentration gradient exists at a site due to heterogeneous soil geological conditions or to surface recharge that imparts a vertical component to groundwater flow.

Dispersion modeling equations for water systems take the same form as those presented later in this chapter for atmospheric-based problems. Analytical solutions are not nearly as complicated or difficult, since the bulk motion of the fluid (in this case, water) is a weak variable with respect to magnitude, direction, time, and position compared to when the fluid is air (i.e., the atmosphere). A variety of analytical, semianalytical, and numerical models and approaches are available for the range of water exposure problems considered earlier, and the reader is referred to the EPA Center for Exposure Assessment Modeling (CEAM; <http://www.epa.gov/ceampubl/index.html>), the Integrated Groundwater Modeling Center (IGMT; <http://igwmc.mines.edu/index.html>), and the EPA Center for Subsurface Modeling Support (CSMoS; <http://epa.gov/ada/csmos/>) for current modeling approaches and procedures.

Illustrative Example 10.3

An oil tanker has collided with a freighter at sea. A rupture on the side of the tanker has released 450,000 gal of crude oil (specific gravity = 0.88) into a "rough" sea. Estimate the spill area of oil resulting from the accident. The oil will float, i.e., it is an LNAPL, since it is lighter than water, forming a monolayer of oil on the sea surface that can be assumed to reach a height, h , in rough seas of 0.05 in.

Solution

The problem is to determine the surface area of the oil spill with this monolayer thickness based on the total volume of oil released from the tanker, assuming no loss of oil through volatilization, dissolution, degradation, etc., shortly after the release. First convert the volume, V , of oil from gallons to cubic feet:

$$V = \frac{450,000 \text{ gal}}{7.48 \text{ gal/ft}^3} = 60,160 \text{ ft}^3$$

If the oil is distributed radially from the point of discharge in the form of a cylinder 0.05 in. high, the radius of spread, r_s , is given by

$$V = \pi (r_s)^2 h$$

Solving for r_s yields:

$$\begin{aligned} r_s &= \left(\frac{V}{\pi h} \right)^{0.5} = \left[\frac{60,160 \text{ ft}^3}{\pi (0.05 \text{ in.} / 12 \text{ in./ft})} \right]^{0.5} \\ &= 2,144 \text{ ft, approximately half a mile} \end{aligned}$$

Illustrative Example 10.4

A leak of trichloroethylene (TCE) has been detected at a landfill at a Superfund site approximately 60 m directly upgradient from the capture zone of the drinking water well of Plainville, MA. Groundwater is moving in the aquifer at a rate of 60 m/year, while the TCE is moving at a retarded velocity one-third that of groundwater in the same direction as the ground water flow. Tangential dispersion can be assumed to be insignificant relative to the axial velocity. Data indicate that the groundwater flow pattern in the aquifer is homogenous and isotropic.

Development of a new potable water supply well will cost \$2,000,000 and will take 6 months. A monitoring well can be installed and operational within 1 month at a cost of \$50,000. Plainville has a tax base of 300 middle and lower middle class households and has very little political clout. Determine how many days it will take the TCE to reach the Plainville's aquifer, and how soon Plainville must decide whether to relocate their wells or not in order to prevent contamination of their water supply.

Solution

The TCE will move from the source of contamination along the projected flow path of the groundwater at a retarded velocity due to its adsorption to organic matter in the aquifer solids. This retarded velocity is

$(60\text{ m/year})/3 = 20\text{ m/year}$. With the direct distance between the TCE and the Plainville water supply along the projected groundwater flow path measuring approximately 60 m, the TCE plume front should reach Plainville in approximately

$$\frac{60\text{ m}}{20\text{ m/year}} = 3\text{ years}$$

In approximately 3 years, the TCE will begin to be intercepted by the water well for Plainville, and concentrations will begin to rise as the plume continues its movement downgradient and toward the city's well. The exact time that the TCE concentration reaches the drinking water maximum contaminant level (MCL) for TCE depends on the source area concentration and the operation of the drinking water well, but within the 3 year period the well is projected to start being contaminated and will only increase in TCE concentration over time. These analyses are based on available data and an assumption that the geological features are uniform in the region surrounding Plainville. The actual time to reach the well capture zone could be reduced if short circuiting occurred through formations not evident in these preliminary survey results. The actual time to reach the well capture zone could be increased if measures are put into place to intercept the TCE plume and treat the contamination at the source. Overall, the city has only a short time to act before their well is contaminated and should take action quickly to prevent well and water supply system contamination from this landfill leak.

10.4 Dispersion in Soils

Few states had regulatory programs for land disposal of hazardous wastes before 1976. However, national awareness of hazardous waste problems increased dramatically in the mid- to late 1970s as it became evident that mismanagement and indiscriminant dumping of hazardous wastes at many sites had led to the release of toxic materials throughout the environment and unacceptable exposures to surrounding communities. Uncontrolled hazardous waste sites are distributed throughout the United States. They occur in various geological settings and in urban as well as rural areas. Uncontrolled sites may be operational, inactive, or abandoned. A wide range of chemical wastes have been deposited at uncontrolled land disposal sites, and the extent and severity of the resulting environment contamination varies greatly across sites.

Many of the factors that influence the extent and overall risk posed by this soil contamination are site specific—either climatic or hydrogeological.

Other factors that influence the extent and severity of contamination relate to land surface features such as topography or development, which can influence the actual disposal methods and transport routes to soils and underlying groundwater. Additional important considerations are the types of chemicals present at a site, the potential for migration, the degree of contamination, and the extent of the area affected. Other significant issues include the location of the site with respect to drinking water sources, population centers, potential social and economic impacts of contamination, and the potential for land redevelopment and reuse.

In the past, the presence of hazardous substances in soils was not a major public concern. In spite of the large number of documented hazardous waste sites in the United States, relatively few sites have been cleaned up with specific redevelopment in mind. Remedial actions usually are undertaken to contain or remove chemical contaminants; little or no consideration is often given to the ultimate use of the site. If land reuse is decided upon before the cleanup, there may be an opportunity to tailor the cleanup activities and final cleanup levels to best suit the end land use (commercial, industrial, and residential) associated with site redevelopment.

The potential for hazardous contaminants in soils to migrate to groundwater or to surface water is often of major concern. Detailed evaluation of cleanup levels frequently involves modeling the movement of contaminants to groundwater or surface water, and estimating the maximum levels in soil that will not interfere with acceptable water quality limits. Drinking water standards and water quality criteria developed by the EPA are widely used as guidance for acceptable levels in water. Water quality standards or criteria developed by individual state environmental agencies also may be applied.

One measure of the significance of contaminants in soil or solid waste samples may be determined by comparing the levels with reported naturally occurring concentrations. Provided levels are within the range that may occur naturally, one might conclude that the sample contaminant levels are of little consequence.

A rigorous treatment of dispersion in soils is beyond the scope of this book. However, some qualitative discussion is warranted because of the potential and existing problems already described. Two main problems arise because dispersion in soil (or land) is anisotropic (i.e., it varies with direction) and the permeability is not only a variable but also an unknown.

The variation in permeability with direction reflects the differences in path length through which a fluid element moves and the forces it experiences in moving through the porous media in a given direction. The governing equation can be reduced to three principal components (as with the diffusion coefficient) by choosing a coordinate system that corresponds to the principal axes of the soil. The anisotropy of a porous medium (like a soil) is undoubtedly related to the internal structure of the medium, and the

structure is related to the circumstances under which the porous media was formed. A porous medium may be expected to be anisotropic if the elementary particles are asymmetric and have, on the average, a particular orientation. Even beds of symmetric particles can be anisotropic if they are present in certain regular patterns. In naturally occurring soils, however, the packing pattern is sufficiently random to preclude the occurrence of anisotropy in beds made up of symmetric particles. The size distribution of the particles making up the bed also can affect the magnitude of the permeability, but ordinarily this does not contribute to the anisotropy.

For beds made up of randomly oriented symmetric particles, the permeability, K , may be estimated by

$$K = \left[\frac{\epsilon^3}{(1 - \epsilon)^2} \right] \left(\frac{d_e^2}{36k} \right) \quad (10.3)$$

with k equal to 5. The equation predicts the permeability reasonably well if the particles are approximately the same size. The hydraulic radius of the bed, d_e , can be estimated from measurements of pore size distribution. The porosity that must be used in this equation is the "effective porosity," ϵ (i.e., the porosity that reflects only the interconnecting flow channels). Typical effective porosities are in the 0.3–0.5 range. Vertical and horizontal permeabilities in soils can range from 1 to $50 \times 10^{-7} \text{ cm}^2$, while average or equivalent particle diameters, d_e , can be as small as $10 \mu\text{m}$.

For 1-D dispersion in soils, the governing equation for a conservative species and/or pollutant, c , in a Cartesian (rectangular) coordinate system moving with velocity, v_x , is given by

$$\frac{\partial c}{\partial t} + v_x \frac{\partial c}{\partial x} = D_L \frac{\partial^2 c}{\partial x^2} \quad (10.4)$$

where D_L is the "effective" dispersion coefficient in the longitudinal direction [5]. For 2-D dispersion, Equation 10.5 is employed:

$$\frac{\partial c}{\partial t} + v_x \frac{\partial c}{\partial x} = D_L \frac{\partial^2 c}{\partial x^2} + D_T \frac{\partial^2 c}{\partial y^2} \quad (10.5)$$

where D_T is the transverse dispersion coefficient [5].

Illustrative Example 10.5

A consulting engineer has been hired by a state agency to perform an exposure assessment at a private dwelling. The dwelling is located over a shallow aquifer that has been contaminated by a gasoline leak from an underground storage tank at the corner gasoline station. List at least

eight important environmental factors that the consulting engineer should consider when visiting the dwelling.

Solution

The following are some of the factors that a consulting engineer should consider in conducting the exposure and risk assessment at this private dwelling:

1. Presence or absence of a basement and, if present, possible ingress routes for liquids and vapors into the basement
2. Ventilation of the dwelling
3. Concentration of the dissolved hydrocarbon fraction in ground-water near the dwelling
4. Presence or absence of separate-phase gasoline near the home
5. Water supply system used by the dwelling's occupants; i.e., are they using a well that taps into the contaminated aquifer, or are they on a municipal water distribution system?
6. Ages, genders, and lifestyles of the dwelling's occupants
7. Concentration of vapors in the zone near or under the house and possible risk of explosion or intoxication
8. If not yet near the dwelling, the rate of transport of dissolved contaminants and separate phase LNAPL toward the dwelling
9. Toxicity and cancer dose-response data for the constituents of the gasoline
10. Estimated additional cancer risk for the dwelling's occupants when exposure data are combined with cancer dose-response data

10.5 Dispersion in the Atmosphere

10.5.1 Effective Height of Atmospheric Emissions

Chemical emissions to the atmosphere can take place from releases at ground level due to tank and pipe ruptures, spills, etc., or from an elevated source such as a stack, vent pipe, etc. To estimate the exposure of these ground level or elevated releases, the "effective" height of a release must be determined as the starting point for its movement downwind toward receptors. The effective height of an emission rarely corresponds to the physical height of the source or the stack. If the plume is caught in the turbulent wake of a stack or of buildings in the vicinity of the source or stack, the plume will be mixed rapidly downward toward the ground. If the plume is emitted free of these turbulent zones, a number of physical and thermal characteristics of the emission source, as well as meteorological factors, influence the rise of the plume. The "effective" height of the emission is estimated employing an applicable plume rise equation that will be presented below.

The chemical's maximum ground level concentration (GLC) may then be determined using an appropriate atmospheric diffusion equation based on this effective height.

The focus for the remainder of this section is on the estimation of the effective height of *stack* emissions that develops because of plume rise considerations. This effective height depends on a number of factors. The emission source factors include the gas flow rate and temperature of the effluent at the top of the stack, as well as the diameter of the stack opening. The meteorological factors influencing plume rise are wind speed, air temperature, wind speed variability with height, and atmospheric stability. No theory on plume rise presently takes into account all these variables, and it appears that the number of formulas for calculating plume rise varies inversely with the technical community's understanding of the process. Most of the equations that have been formulated for computing the effective height of an emission are semiempirical. When considering these "plume rise" equations, it is important to evaluate each one in terms of the assumptions made and the circumstances existing when the particular correlation was formulated. Depending on the circumstances, some equations may be more applicable than others for a given application.

The effective stack height, H^* (equivalent to the effective height of the emission), is usually considered as the sum of the actual stack height, H_s , plus the plume rise, Δh , due to the velocity (momentum) of the issuing gases and the buoyancy rise, which is a function of the temperature of the gases being emitted and the surrounding atmospheric conditions. Three key equations are provided below.

The Davidson–Bryant method is empirical because it is based on Bryant's wind tunnel experiments [6]. It is restricted to gases below 125°F and to stacks of moderate height and larger. It does not give the maximum plume rise because it is a function of momentum only, not buoyancy. The method applies when the atmosphere neither resists nor assists the vertical motion of the plume and when wind velocities are 20 mph or higher. It is above this wind velocity that the vertical vector of the stack discharge velocity is insignificant compared with the horizontal wind velocity vector. The governing equation is given by

$$\Delta h = D_s \left(\frac{v_s}{u} \right)^{1.4} \left[1.0 + \left(\frac{T_G - T_a}{T_G} \right) \right] \quad (10.6)$$

where

Δh is the rise of the plume above the stack, m

D_s is the inside diameter of the stack, m

v_s is the stack exit velocity, m/s

u is the wind speed, m/s

T_G is the stack gas temperature, K

T_a is the ambient air temperature, K

The Holland equation (see Equations 10.7 and 10.8) is valid for effluent gases hotter than 125°F and for neutral conditions [7]:

$$\Delta h = \frac{1}{u} (1.5v_s D_s + 0.04Q_H) \quad (10.7)$$

$$Q_H = \left(\frac{\pi d_s^2 v_s}{4} \right) \left[\frac{P}{R/MW} \right] c_p \left(\frac{T_G - T_a}{T_G} \right) \quad (10.8)$$

where

Q_H is the heat emission rate of the stack, kcal/s

P is the atmospheric pressure, dynes/m²

R is the universal gas constant, 1833.35 dyne-m/K-gmol

MW is the molecular weight of the effluent, g/gmol

c_p is the heat capacity of the effluent gas at constant pressure, kcal/g-K

A more popular form of Equation 10.7 is

$$\Delta h = \left(\frac{v_s D_s}{u} \right) \left[1.5 + 2.68 \times 10^{-3} P \left(\frac{T_G - T_a}{T_G} \right) D_s \right] \quad (10.9)$$

where P is the atmospheric pressure, mbars. Holland's equation frequently underestimates the effective height of emission; therefore, its use often provides a slight safety factor. Holland also suggests that a value between 1.1 and 1.2 times Δh from the equation should be used for unstable conditions; a value between 0.8 and 0.9 times the Δh from the equation should be used for stable conditions. Since plume rise from a stack occurs over some distance downwind, Equation 10.9 should not be applied within the first few hundred meters of the stack.

In view of the stability class definitions given in Table 10.1, Briggs used the following equations to calculate the plume rise for unstable or neutral conditions [8]:

TABLE 10.1

Stability Class Definitions

Stability	Type	Potential Temperature Lapse Rate (K/100 m) ^a , $\Delta\theta/\Delta z$
0	Unstable	$\Delta\theta/\Delta z < -0.22$
1	Neutral	$-0.22 \leq \Delta\theta/\Delta z < 0.15$
2	Neutral	$0.15 \leq \Delta\theta/\Delta z < 0.85$
3	Stable	$0.85 \leq \Delta\theta/\Delta z$

^a $\theta = T + 0.0098z$, where T is in Kelvin and z in meters.

$$\Delta h = 1.6(F)^{1/3}(u)^{-1}(x)^{2/3}; \text{ if } x < x_f \quad (10.10)$$

$$\Delta h = 1.6(F)^{1/3}(u)^{-1}(x_f)^{2/3}; \text{ if } x > x_f \quad (10.11)$$

$$x^* = 14(F)^{5/8}; \text{ when } F < 55 \text{ m}^4/\text{s}^3 \quad (10.12)$$

$$x^* = 34(F)^{2/5}; \text{ when } F > 55 \text{ m}^4/\text{s}^3 \quad (10.13)$$

$$x_f = 3.5x^* \quad (10.14)$$

where

F is the buoyancy flux = $3.7 \times 10^{-5} (Q_H)_i$, m^4/s^3

Q_H is the heat emission, cal/s

x is the downwind distance, m

x^* is the distance of transition from first stage of rise to the second stage of rise, m

x_f is the distance to final rise, m

The term F may be estimated (if Q_H is not available) by:

$$F = \frac{(g/\pi)(V)(T_s - T)}{T_s} \quad (10.15)$$

where

g is the gravitational acceleration, 9.8 m/s^2

V is the stack gas volumetric flow rate, m^3/s

T_s and T are the stack gas and the ambient air temperature, respectively, K

For stable conditions, the potential temperature lapse rate, $\Delta\theta/\Delta z$, is needed. If $\Delta\theta/\Delta z$ is not given, one may use 0.02 K/m for Stability Class E and 0.035 K/m for Stability Class F. Stability categories and conditions are described in more detail in the next section. The term

$$s = \frac{g(\Delta\theta/\Delta z)}{T} \quad (10.16)$$

can be used to calculate plume rise for stable conditions using both Equations 10.17 and 10.18:

$$\Delta h = 2.4 \left(\frac{F}{us} \right)^{1/3} \quad (10.17)$$

$$\Delta h = \frac{5F^{1/4}}{s^{3/8}} \quad (10.18)$$

The smaller of these two Δh s should be used; it represents the final plume rise. The distance to final rise is given by Equation 10.19 for stable conditions:

$$x_f = \frac{3.14u}{s^{1/2}} \quad (10.19)$$

To calculate the rise for stable conditions for a downwind distance x less than x_f , one may employ

$$\Delta h = \frac{1.6F^{1/3}x^{2/3}}{u} \quad (10.20)$$

which is the same equation used for unstable and neutral conditions.

In 1972, the Tennessee Valley Authority (TVA) reported on a comprehensive study they conducted to develop procedures for estimating plume rise at specific distances, x , downwind from coal-fired power plant stacks [9]. This study developed plume rise equations for three meteorological conditions as follows. For neutral atmospheric stability conditions defined by $-0.17 \text{ K}/100 \text{ m} < \Delta\theta/\Delta z < 0.16 \text{ K}/100 \text{ m}$ and distances up to 3000 m downwind, Equation 10.21 applies:

$$\Delta h = \frac{2.50x^{0.56}F^{1/3}}{u} \quad (10.21)$$

For moderately stable atmospheric conditions defined by $0.16 \text{ K}/100 \text{ m} < \Delta\theta/\Delta z < 0.70 \text{ K}/100 \text{ m}$ and distances up to 2800 m downwind, Equation 10.22 applies:

$$\Delta h = \frac{3.75x^{0.49}F^{1/3}}{u} \quad (10.22)$$

Finally, for very stable atmospheric conditions where $0.70 \text{ K}/100 \text{ m} < \Delta\theta/\Delta z < 1.87 \text{ K}/100 \text{ m}$ for distances downwind up to 1960 m, Equation 10.23 is used:

$$\Delta h = \frac{13.8x^{0.26}F^{1/3}}{u} \quad (10.23)$$

Many more plume rise equations may be found in the literature.

Illustrative Example 10.6

A proposed source is to emit 72 g/s of a toxic chemical from a stack 30 m high (h) with a diameter (D_s) of 1.5 m. The effluent gases are emitted at a temperature of 250°F (394 K) with an exit velocity (v_s) of 13 m/s. Using Holland's plume rise equation (Equation 10.9), obtain the plume rise (Δh) as a function of wind speed for Stability Classes B (unstable) and D (neutral). Also calculate the effective height, H^* . Assume that the design atmospheric pressure is 970 mbar and that the design ambient air temperature is 20°C (293 K). Also assume that Holland's correction factor for Stability Classes B and D are 1.15 and 1.0, respectively.

Solution

Substituting values given in the problem statement into Holland's equation (Equation 10.9) gives an uncorrected plume rise estimate as a function of wind speed at the stack exit of:

$$\begin{aligned}\Delta h &= \frac{(13 \text{ m/s})(1.5 \text{ m})}{u} \left[1.5 + 2.68 \times 10^{-3} (970 \text{ mbar}) \left(\frac{394 - 293 \text{ K}}{394 \text{ K}} \right) (1.5 \text{ m}) \right] \\ &= \frac{48.8}{u} \text{ m}\end{aligned}$$

For Stability Class B, the unstable atmospheric condition, this Δh expression would be multiplied by 1.15, while for Stability Class D, the neutral atmospheric condition, the plume rise expression should be multiplied by 1.0. The effective stack height for the Stability Class B case is as follows:

$$H^* = h + \Delta h = 30 \text{ m} + 1.15 \left(\frac{48.8}{u} \right) \text{ m}$$

Both the plume rise and the effective stack height for various wind speeds and stability classes are summarized in Table 10.2.

10.5.2 Atmospheric Dispersion Equations for Continuous Sources

There are many dispersion equations available, most of them semiempirical. It is not the intent of this section to develop each in detail but rather to look at the one that has found the greatest applicability today. In the authors' opinion, the best atmospheric dispersion workbook published to date is that by Turner [7].

The coordinate system used in making the atmospheric dispersion estimates as suggested by Pasquill and modified by Gifford [7] is shown in Figure 10.1. (Note that this is the coordinate system used by most engineers.) The origin is placed at ground level at or beneath the point of emission, with

TABLE 10.2
Summary of Stack Height H^* (m) for Nine Wind
Speeds u (m/s) and Class D and B Stabilities
(Illustrative Example 10.6)

u	Class D		Class B	
	Δh	$H^* = H_s + \Delta h$	$1.15 \Delta h$	$H^* = H_s + 1.15 \Delta h$
0.5	97.6	127.6	112.2	142.2
1.0	48.8	78.8	56.1	86.1
1.5	32.6	62.6	37.5	67.5
2	24.4	54.4	28.1	58.1
3	16.3	46.3	18.7	48.7
5	9.8	39.8	11.3	41.3
7	7.0	37.0	8.0	38.0
10	4.9	34.9		
20	2.4	32.4		

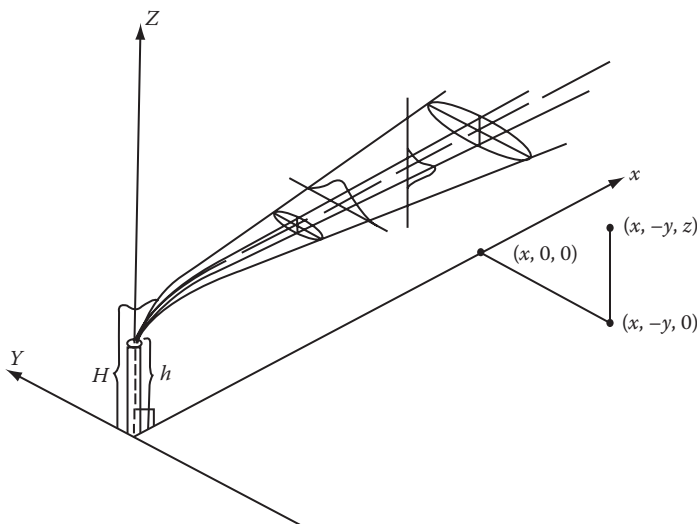


FIGURE 10.1
Coordinate system showing Gaussian distributions in the horizontal and vertical.

the x -axis extending horizontally in the direction of the mean wind velocity. The y -axis is in the horizontal plane perpendicular to the x -axis, while the z -axis extends vertically in a positive direction from the ground surface. The plume travels along or parallel to the x -axis (in the mean wind direction) at a mean velocity equal to the mean wind speed, u .

The concentration, c , of a gas or aerosol at (x, y, z) from a continuous source with an effective emission height, H^* , is given by

$$c(x, y, z; H^*) = \frac{q}{2\pi\sigma_y\sigma_z u} \left\{ \exp \left[-\frac{1}{2} \left(\frac{y}{\sigma_y} \right)^2 \right] \right\} \left\{ \left[-\frac{1}{2} \left(\frac{z - H^*}{\sigma_z} \right)^2 \right] + \exp \left[-\frac{1}{2} \left(\frac{z + H^*}{\sigma_z} \right)^2 \right] \right\} \quad (10.24)$$

where

q is the pollutant mass emission rate, g/s

σ_y and σ_z are dispersion coefficients in the y and z directions, respectively, m

The assumptions made in the development of Equation 10.24 are

1. The plume spread has a Gaussian distribution in both the horizontal and vertical planes with standard deviations of plume concentration distribution in the horizontal and vertical of σ_y and σ_z , respectively.
2. The emission rate of the pollutant, q , is constant.
3. Total reflection of the plume takes place at the earth's surface, and the plume moves downwind with mean wind speed u .

Although any consistent set of units may be used, the cgs system is preferred.

Equation 10.24 is valid where diffusion in the direction of plume travel can be neglected (i.e., there is no diffusion in the x direction). This is a valid assumption if the release is continuous or if the duration of the release is equal to or greater than the travel time, x/u , from the source to the receptor of interest.

For concentrations calculated at ground level ($z=0$), Equation 10.24 simplifies to:

$$c(x, y, 0; H^*) = \frac{q}{\pi\sigma_y\sigma_z u} \left\{ \exp \left[-\frac{1}{2} \left(\frac{y}{\sigma_y} \right)^2 \right] \right\} \left\{ \exp \left[-\frac{1}{2} \left(\frac{H^*}{\sigma_z} \right)^2 \right] \right\} \quad (10.25)$$

Where the concentration is to be calculated along the centerline of the plume at $y=0$, further simplification of Equation 10.25 gives:

$$c(x, 0, 0; H^*) = \frac{q}{\pi\sigma_y\sigma_z u} \left\{ \exp \left[-\frac{1}{2} \left(\frac{H^*}{\sigma_z} \right)^2 \right] \right\} \quad (10.26)$$

In the case of a ground level source with no effective plume rise, i.e., $H^*=0$, then Equation 10.26 simplifies even further to yield:

$$c(x, 0, 0; 0) = \frac{q}{\pi \sigma_y \sigma_z u} \quad (10.27)$$

The values of σ_y and σ_z vary with the turbulent structure of the atmosphere, the height above the surface, the surface roughness, the sampling time over which the concentration is to be estimated, the wind speed, and the distance from the source. For the parameter values that follow, the sampling time was originally assumed to be about 10 min, the height to be the lowest several hundred meters of the atmosphere, and the surface to be relatively open country. The parameters are estimated from the stability of the atmosphere, which is, in turn, estimated from the wind speed at a height of about 10 m and, during the day, the incoming solar radiation or, during the night, the amount of cloud cover. Stability categories are given in Table 10.3. Note that A, B, and C refer to daytime stability classes with unstable atmospheric conditions; Stability Class D refers to overcast or neutral conditions at night or during the day; and Stability Classes E and F refer to nighttime stable conditions and are based on the amount of cloud cover that is present. "Strong" incoming solar radiation corresponds to a solar altitude greater than 60° with clear skies (e.g., sunny midday in midsummer); "slight" insolation (rate of radiation from the sun received per unit of earth's surface) corresponds to a solar altitude from 15° to 35° with clear skies (e.g., sunny midday in midwinter). For the A–B, B–C, and C–D stability categories, use the average of the A and B values, B and C values, and C and D values, respectively.

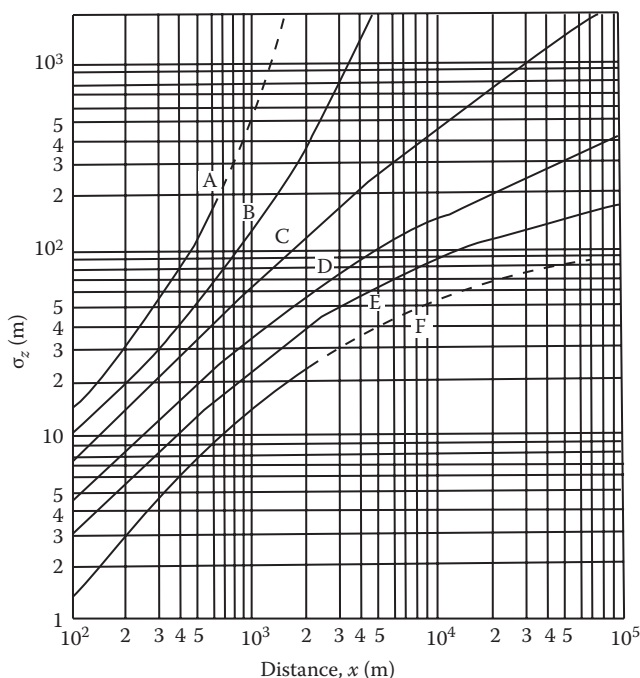
Having determined the stability class, Figures 10.2 and 10.3 may then be used to evaluate σ_y and σ_z , respectively, as a function of downwind distance from the source. Figures 10.2 and 10.3 strictly apply to open, flat terrain and generally underestimate the plume dispersion potential from low-level

TABLE 10.3

Stability Categories

Surface Wind Speed at 10 m (m/s)	Day			Night	
	Incoming Solar Radiation			Thinly Overcast or ≥ 4/8 Low Cloud	
	Strong	Moderate	Slight	≤3/8 Cloud	
2	A	A–B	B		
2–3	A–B	B	C	E	F
3–5	B	B–C	C	D	E
5–6	C	C–D	D	D	D
6	C	D	D	D	D

Class A is the most unstable, and Class F is the most stable. The Neutral Class, D, should be assumed for overcast conditions during the day or the night, regardless of wind speed. Night refers to the period from 1 h before sunset to 1 h after sunrise.

**FIGURE 10.2**

Vertical dispersion coefficient as a function of downwind distance from the source; A–F designate stability categories listed in Table 10.3.

sources in built-up areas. Although the vertical spread may be less than the values for Class F with very light winds on a clear night, quantitative estimates of concentrations are nearly impossible for this condition. With very light winds on a clear night for ground level sources free of topographic influences, frequent shifts in wind direction usually occur, which serve to spread the plume horizontally. For elevated sources under these extremely stable situations, significant concentrations usually do not reach the ground level until the stability changes. It is important to note that Equation 10.24, as well as the emergency dispersion models and equations presented later in this chapter (and further discussed in Part III), can be used to calculate the concentration profile of a pollutant, including hazardous and/or toxic substances. If the pollutant is explosive, a “vapor cloud profile” can be calculated where the vapor cloud would contain concentrations in the explosive range.

The effect of multiple-stack sources has been handled in the past by simply treating each as a distinct source and adding the resulting concentrations to obtain the total concentration. Probably the best method now available for estimating the effect of multiple sources is that suggested by TVA [10]. Using their approach for the case of multiple stacks, all having the same height, one estimates the concentration for a single stack and then multiplies this result

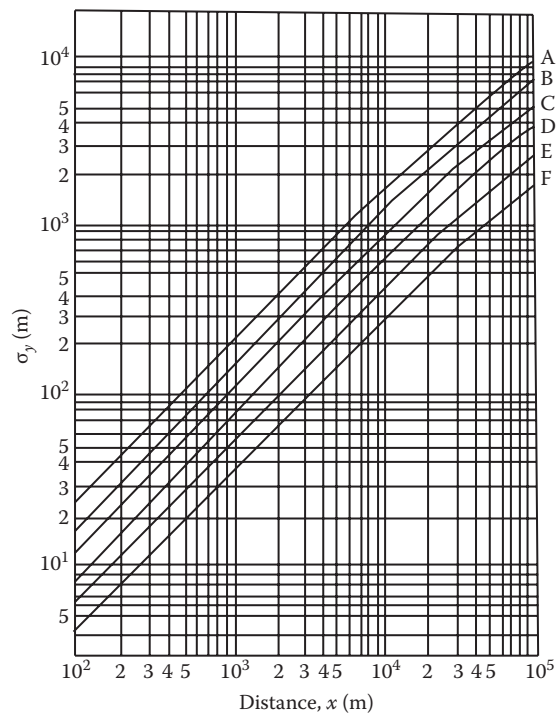


FIGURE 10.3
Transverse dispersion coefficient as a function of downwind distance from the source; A–F designate stability categories listed in Table 10.3.

by the factor provided in Table 10.4 corresponding to the total number of stacks of this size.

Stack emissions can include particulates as well as dense gases (heavier than air, e.g., chlorine). These emissions are subjected to a downwash as they settle through the atmosphere due to the force of gravity. For particles,

TABLE 10.4
Multiple-Stack Source Factors

Number of Stacks of a Given Height	Multiplication Factor
2	1.7
3	2.41
4	3.0
5	3.6
6	4.2
7	4.71
8	5.3
9	5.8
10	6.3

especially large ones, an additional external force term must be included in the prediction of plume concentration. A rather simple approach for particles is to assume no reflection of particles back into the lower atmosphere and to superimpose their settling velocity as a vertical velocity component on the initial point of discharge to change their effective height over time in the following manner:

$$c = \frac{q}{2\pi\sigma_y\sigma_z u} \exp \left\{ -\frac{1}{2} \left[\left(\frac{y}{\sigma_y} \right)^2 + \left(\frac{z-H^*}{\sigma_z} \right)^2 \right] \right\} \quad (10.28)$$

where H^* in Equation 10.28 = $H - vx/u$, and v is the terminal settling velocity of the particle in question, m/s. This effectively “repositions” the particle vertically as it moves downstream from the source and eliminates the need for developing and solving a revised equation. If Equation 10.28 is used to calculate ground level ($z=0$), centerline ($y=0$) concentrations, Equation 10.29 results:

$$c = \frac{q}{2\pi\sigma_y\sigma_z u} \exp \left[-\frac{1}{2} \left(\frac{H^*}{\sigma_z} \right)^2 \right] \quad (10.29)$$

The rate of deposition of particles per unit area, R , is then given by the product of the local GLC and the terminal vertical settling velocity of the particle, i.e.:

$$R = cv = \frac{qv}{2\pi\sigma_y\sigma_z u} \exp \left[-\frac{1}{2} \left(\frac{H^*}{\sigma_z} \right)^2 \right] \quad (10.30)$$

A consistent set of SI units is g/s-m² for R , g/s for q , m/s for v and u , and m for σ and H^* .

The terminal settling velocity is usually given by [11]:

$$v = \frac{(gd_p^2\rho_p)}{18\mu_g} C \quad (10.31)$$

where

g is the acceleration due to gravity, m/s²

d_p is the particle diameter, m

ρ_p is the particle density, g/m³

μ_g is the viscosity of air, g/m-s

C is the Cunningham correction factor, that can be reasonably approximated by [12]:

$$C = 1 + \frac{9.73 \times 10^{-3} T^{1/2}}{d_p} \quad (10.32)$$

where

d_p is the particle diameter, μm

T is the temperature, K

It is important to note that the deposition rate is a strong function of particle diameter through the term v , which appears twice in the deposition flux equation. The previous equations must be modified to treat process gas streams discharging particles of a given size distribution. The suggested procedure is somewhat similar to that for calculating overall collection efficiencies for particulate control equipment [11,13]. For this condition, the overall rate is given by:

$$R = \sum_{i=1}^n \left(\frac{q_i v_i}{2\pi u \sigma_y \sigma_z} \right) \exp \left[-\frac{1}{2} \left(\frac{H_i^*}{\sigma_z} \right)^2 \right] \quad (10.33)$$

where

i is the size range in question for a particle size distribution divided into n size ranges

q_i is the discharge rate of particles in size range i

v_i is the settling velocity of particles evaluated at the average particle size in size range i

H_i^* is the corrected effective height evaluated for the average particle size in size range i

To this point, the development of atmospheric dispersion equations has been limited to emissions from a "point" (e.g., stack) source. Although most dispersion applications involve point sources, in some instances the location of the emission can be more accurately described physically and mathematically by either a line source or an area source.

Line sources are generally confined to roadways and streets along which there are well-defined movements of motor vehicles. For these sources, data are required on the width of the roadway and its center strip, the types and amounts (g/s-m) of pollutant emissions, the number of lanes, the emissions from each lane, and the height of the emissions. In some situations (e.g., a traffic jam at a tollbooth, a series of industries located along a river, and heavy traffic along a straight stretch of highway), the dispersion problem may be modeled as a continuous emitting infinite line source. GLCs downwind of a continuously emitting infinite line source, when the wind direction is perpendicular to the line source, can be calculated from

$$c(x,y,0; H^*) = \frac{2q'}{\sqrt{2\pi} \sigma_z u} \exp \left[-\frac{1}{2} \left(\frac{H^*}{\sigma_z} \right)^2 \right] \quad (10.34)$$

Here, q' is the source strength per unit distance (e.g., g/s-m). Note that the horizontal dispersion parameter, σ_y , does not appear in this equation since it is assumed that lateral dispersion from one segment of the line is compensated by dispersion in the opposite direction from adjacent segments. Also, y does not appear since the concentration at a given x is the same for any value of y . Concentrations from infinite line sources, when the wind is not perpendicular to the line, can also be approximated using Equation 10.35. If the angle between the wind direction and the line source is ϕ , Equation 10.34 can be written as:

$$c(x,y,0; H^*) = \frac{2q'}{\sin \phi \sqrt{2\pi} \sigma_z u} \exp \left[-\frac{1}{2} \left(\frac{H^*}{\sigma_z} \right)^2 \right] \quad (10.35)$$

This equation should not be used where ϕ is less than 45° .

When the continuously emitting line source is reasonably short or "finite," the edge effects caused by the two ends of the source can be accounted for. If the line source is perpendicular to the wind direction, it is convenient to define the x -axis in the direction of the wind, passing through the sampling point downwind. The ends of the line source then are at two positions in the crosswind direction, y_1 and y_2 , where y_1 is less than y_2 . The concentration along the x -axis at ground level is then given by:

$$c(x,0,0; H^*) = \frac{2q'}{\sqrt{2\pi} \sigma_z u} \left\{ \exp \left[-\frac{1}{2} \left(\frac{H^*}{\sigma_z} \right)^2 \right] \right\} \left\{ \int_{p_1}^{p_2} \frac{1}{\sqrt{2\pi}} \left(\exp \left(-\frac{1}{2} p^2 \right) dp \right) \right\} \quad (10.36)$$

where $p_1 = y_1/\sigma_y$ and $p_2 = y_2/\sigma_y$. Once the limits of integration have been established, the value of the integral may be determined from standard tables of integrals.

Area sources include the multitude of minor sources with individually small emissions that are impractical to consider as a separate point or line sources. Area sources are typically treated as a grid network of square areas, with pollutant emissions distributed uniformly within each grid square. Area source information required includes types and amounts of pollutant emissions, the physical size of the area over which emissions are distributed, and representative height for the area. In dealing with dispersion of pollutants in areas having large numbers of sources (e.g., as in fugitive dust from coal piles, a large number of automobiles in a parking lot, or a multipool situation), there may be too many sources to consider each source

individually [14]. Often an approximation can be made by combining all the emissions into a given square area and treating this area as a virtual point source having a horizontal standard deviation, σ_{y0} , approximated by $\sigma_{y0} = s/4.3$, where s is the length of a side of the area. A virtual distance, x_y , can then be found that will give this standard deviation for a given stability class, i.e., the distance that will yield the appropriate value for σ_y from Figure 10.3. The equations for a point source may then be used to estimate downwind concentrations, and determining σ_y as a function of $x + x_y$. This procedure effectively treats the area source as a crosswind line source with a normal distribution for pollutant concentration; this is a fairly good approximation for the distribution across an area source. If the emissions within an area are from varying effective stack heights, the variation may be approximated by determining an upwind location for the virtual point source for a given stability class using a σ_{z0} value for the vertical distribution of the combined sources. Thus, point source equations would be used for estimating concentrations downwind from this virtual point source, determining σ_z as a function of $x + x_z$.

It should be noted that the practicing engineer or scientist may use any model as long as

1. The modeler uses applicable parameters specified in the relevant air quality rules.
2. The modeler uses applicable definitions of worst-case scenarios.
3. The model is appropriate for the chemicals and conditions being modeled.
4. The model is publicly or commercially available or is a proprietary model that the modeler is willing to share with EPA.

Typical EPA recommended models include:

1. DEGADIS (accidental releases)
2. SCREEN3 (screening level steady-state emissions)
3. ALOHA (accidental releases)
4. ISC3 (steady-state emissions)

The choice of any of the dozens of other models available in the literature will depend on the specifics of the source and the applicable information available for meteorological conditions, receptors, terrain, etc., relevant for the scenarios being modeled.

Illustrative Example 10.7

A landfill is assumed to be a ground level source of methane emissions with an emission rate of $100 \text{ g CH}_4/\text{s}$. The Stability Class is C, and the

wind is blowing at 4 m/s from the west. What would the GLC be directly downwind at a receptor site 500 m from the source? If the landfill had an effective stack height of 50 m and all other conditions were the same, what would the ground level, centerline, downwind concentration be at the receptor?

Solution

For this example, the following input values apply:

$$q = 100 \text{ g/s}, u = 4 \text{ m/s}, x = 500 \text{ m}, y = 0 \text{ m}, z = 0 \text{ m}, H^* = 0 \text{ m}$$

From Figures 10.2 and 10.3, the corresponding dispersion coefficients at $x = 500 \text{ m}$ for Stability Class C are found to be:

$$\sigma_y \approx 58 \text{ m}; \sigma_z \approx 35 \text{ m}$$

The GLC given by Equation 10.27 is:

$$\begin{aligned} c(500, 0, 0; 0) &= \frac{q}{\pi \sigma_y \sigma_z u} = \left(\frac{100 \text{ g/s}}{\pi (58 \text{ m})(35 \text{ m})(4 \text{ m/s})} \right) \\ &= \frac{100 \text{ g/s}}{25,210 \text{ m}^3/\text{s}} = 3.97 \times 10^{-3} \text{ g/m}^3 \end{aligned}$$

For an effective stack height, $H^* = 50 \text{ m}$, Equation 10.26 is used, yielding the following concentration:

$$\begin{aligned} c(500, 0, 0; 50) &= \frac{q}{\pi \sigma_y \sigma_z u} \left\{ \exp \left[-\frac{1}{2} \left(\frac{H^*}{\sigma_z} \right)^2 \right] \right\} \\ &= \left(\frac{100 \text{ g/s}}{\pi (58 \text{ m})(35 \text{ m})(4 \text{ m/s})} \right) \exp \left[-\frac{1}{2} \left(\frac{50 \text{ m}}{35 \text{ m}} \right)^2 \right] \\ c(500, 0, 0; 50) &= 3.97 \times 10^{-3} (0.36) = 1.43 \times 10^{-3} \text{ g/m}^3 \end{aligned}$$

As expected, the concentration is lower for an elevated source compared to an equivalent ground source emission.

Illustrative Example 10.8

A malfunction in the control system of a refinery facility has opened a vent to a bypass stack that is emitting uncontrolled chemicals of concern from the refinery. A maximum GLC of $1.7 \times 10^{-3} \text{ g/m}^3$ results 600 m directly downwind from the vent stack that has an effective

height of 50 m. The Stability Class is C. What is the probable vent source strength, g/s, if the mean wind speed is 5 m/s?

Solution

For this example, the given input values are:

$$c(\max) = 1.7 \times 10^{-3} \text{ g/s}, \quad x = 600 \text{ m}, \quad y = 0 \text{ m}, \quad z = 0 \text{ m},$$

$$u = 5.0 \text{ m/s}, \quad H^* = 50 \text{ m}$$

For Stability Class C at $x=600$ m, Figures 10.2 and 10.3 yield the following dispersion coefficient values:

$$\sigma_y \approx 68 \text{ m}; \quad \sigma_z \approx 42 \text{ m}$$

Equation 10.26 can be rearranged and solved for q as follows:

$$c(600,0,0; 50) = \frac{q}{\pi \sigma_y \sigma_z u} \left\{ \exp \left[-\frac{1}{2} \left(\frac{H^*}{\sigma_z} \right)^2 \right] \right\};$$

$$q = \frac{c(600,0,0; 50)(\pi \sigma_y \sigma_z u)}{\{\exp[-1/2(H^*/\sigma_z)^2]\}}$$

Substituting,

$$q = \frac{(1.7 \times 10^{-3} \text{ g/m}^3)(\pi)(68 \text{ m})(42 \text{ m})(5.0 \text{ m/s})}{\exp[-1/2(50/42)^2]}$$

$$= \frac{76.27 \text{ g/s}}{0.492} = 155 \text{ g/s}$$

Illustrative Example 10.9

An incinerator stack is emitting fly ash at a rate of 2 T/h. Natural processes are capable of removing these particles from the affected ground surface at a steady rate, provided no more than 0.02% of the ground is covered by them per hour. The particles are, on the average, spheres of radius 10^{-4} ft and have an average density of 120 lb/ft³. The wind speed is 5 mph. If L is the distance through which an average particle is carried by the wind, the particles will settle out uniformly over a wedge-shaped area whose central angle is 20°, at distances ranging from 0.5 to 20 L . Determine the minimum stack height, H , required to prevent ground level accumulation above the allowable level. Assume monolayer deposition, with the ground area covered by a particle equal to its cross-sectional area [i.e., $\pi(d_p)^2/4$].

Solution

Select 1.0 h as a basis for the calculations. The volume of one particle, V_p , is:

$$V_p = \frac{4}{3}\pi r_p^3 = \frac{4}{3}\pi(10^{-4} \text{ ft})^3 = 4.189 \times 10^{-12} \text{ ft}^3$$

The mass (weight) of one particle is:

$$\text{Mass} = \rho_p V = 120 \text{ lb/ft}^3 (4.189 \times 10^{-12} \text{ ft}^3) = 5.027 \times 10^{-10} \text{ lb}$$

The number of particles emitted per hour is:

$$\begin{aligned} \text{Number of particles emitted} &= \frac{(2T / \text{h})(2000 \text{ lb}/T)}{(5.027 \times 10^{-10} \text{ lb/particle})} \\ &= \frac{(4000 \text{ lb/h})}{(5.027 \times 10^{-10} \text{ lb/particle})} \\ &= 7.96 \times 10^{12} \text{ particles/h} \end{aligned}$$

The area covered by particles per hour is:

$$\begin{aligned} \text{Area covered/h} &= (\text{Number of particles/h}) \left(\frac{\text{Area}}{\text{Particle}} \right) \\ &= (\text{Number of particles/h}) \left(\frac{\pi d_p^2}{4} \right) \\ \text{Area covered/h} &= (7.96 \times 10^{12} \text{ particles/h}) \left[\frac{\pi(2 \times 10^{-4})^2}{4} \text{ ft}^2 \right] \\ &= 250,070 \text{ ft}^2/\text{h} \end{aligned}$$

The wedge-shaped area of particle deposition can be defined as:

$$\text{Deposition area} = \pi[(20L)^2 - (0.5L)^2] \left(\frac{20}{360} \right) = 69.77L^2$$

The allowable loading represents 0.02% of this depositional area or:

$$\text{Allowable loading} = (2 \times 10^{-4})(69.77L^2) = 1.4 \times 10^{-2} L^2 \text{ ft}^2/\text{h}$$

Equating the area covered/h to this allowable loading yields a value for L of the average distance traveled by these emitted particles of:

$$250,070 \text{ ft}^2/\text{h} = 1.4 \times 10^{-2} L^2 \text{ ft}^2/\text{h}, L^2 = 1.79 \times 10^7 \text{ ft}^2, L = 4,226 \text{ ft}$$

The Stokes region applies for the settling of these particles [11]. According to Equation 10.31:

$$v = \frac{(gd_p^2\rho_p)}{18\mu_g} C = \frac{(32.2 \text{ ft/s}^2)(2 \times 10^{-4} \text{ ft})^2(120 \text{ lb/ft}^3)}{18(1.25 \times 10^{-5} \text{ lb/ft-s})} C = 0.687 C \text{ ft/s}$$

The Cunningham correction factor, C , for a particle with diameter 0.0002 ft is determined from Equation 10.32. For this equation, the particle diameter must first be converted to μm as:

$$d_p = (0.0002 \text{ ft})(30.54 \text{ cm/ft})(10^4 \mu\text{m/cm}) = 61.1 \mu\text{m}$$

Assuming an ambient temperature of $20^\circ\text{C} = 293 \text{ K}$, the value of C is:

$$C = 1 + \frac{9.73 \times 10^{-3}(293)^{1/2}}{(61.1)} = 1 + 0.00016 = 1.00016 \approx 1.0$$

indicating that no correction is necessary for the calculation of settling velocity for this large of a particle. The residence time of the particle during settling, t , is given by:

$$t = \frac{L}{u} = \frac{H}{v}; \quad \frac{H}{L} = \frac{v}{u}$$

$$\frac{H}{L} = \frac{0.698 \text{ ft/s}}{(5.0 \text{ miles/h})(5280 \text{ ft/mile})(1 \text{ h}/3600 \text{ s})} = \frac{0.698 \text{ ft/s}}{7.33 \text{ ft/s}} = 0.0952$$

Since $L = 4200 \text{ ft}$,

$$H = (0.0952)(4200) = 400 \text{ ft}$$

Illustrative Example 10.10

An inventory of SO_2 emissions has been conducted in an urban area by square areas, 5000 ft (1524 m) on a side. The emissions from one such area are estimated to be 6 g/s for the entire area. This square is composed of residences and a few small commercial establishments. What is the concentration resulting from this area at the center of the adjacent square to the north on a thinly overcast night when the wind velocity is 2.5 m/s from the south? The average effective stack height of these sources is assumed to be 20 m.

Solution

A thinly overcast night with a wind speed of 2.5 m/s suggests Stability Class E (see Table 10.3). (Conditions may actually be more unstable, since this is a built-up area.) To allow for the area source, let $\sigma_{y0} = 1524 \text{ m}/4.3 = 354 \text{ m}$. For Class E from Figure 10.3, the virtual distance $x_y \approx 8000 \text{ m}$ for a $\sigma_y = 354 \text{ m}$. To calculate the concentration at the center of the adjacent square, $x = 1524 \text{ m}$. To determine the corresponding σ_y value for the virtual point source, $x + x_y = 1524 \text{ m} + 8000 \text{ m} = 9524 \text{ m}$. At 9524 m, $\sigma_y \approx 410 \text{ m}$, $\sigma_z \approx 80 \text{ m}$ (from Figure 10.2).

To determine the centerline, GLC of SO_2 from this virtual elevated point source, Equation 10.26 is applied by substituting the appropriate input values for this problem as:

$$\begin{aligned} c(9524, 0, 0; 20) &= \frac{q}{\pi \sigma_y \sigma_z u} \left\{ \exp \left[-\frac{1}{2} \left(\frac{H^*}{\sigma_z} \right)^2 \right] \right\} \\ &= \left(\frac{6 \text{ g/s}}{\pi (410 \text{ m})(80 \text{ m})(2.5 \text{ m/s})} \right) \exp \left[-\frac{1}{2} \left(\frac{20 \text{ m}}{80 \text{ m}} \right)^2 \right] \\ c(9254, 0, 0; 20) &= 2.33 \times 10^{-5} (0.969) = 2.26 \times 10^{-5} \text{ g/m}^3 \end{aligned}$$

Illustrative Example 10.11

An estimate is required of the total hydrocarbon concentration 300 m downwind of an expressway on an overcast day with wind speed of 4 m/s. The expressway runs north–south and the wind is from the west. The measured traffic flow is 8000 vehicles/h during rush hour, and the average speed of the vehicles is 40 mph. At this speed, the average vehicle is expected to emit $2 \times 10^{-2} \text{ g/s}$ of total hydrocarbons.

Solution

The expressway may be considered to be a continuous, infinite line source. To obtain a source strength q' with units of g/s-m, the number of vehicles/m of highway must be calculated and multiplied by the emission per vehicle as follows:

$$\begin{aligned} \text{Vehicles/m} &= \frac{(8000 \text{ vehicles/h})}{[(40 \text{ miles/h})(1610 \text{ m/mile})]} \\ &= 0.125 \text{ vehicles/m of highway} \end{aligned}$$

The resulting line source strength then is

$$\begin{aligned} q' &= (0.125 \text{ vehicle/m highway}) (2 \times 10^{-2} \text{ g/s hydrocarbons/vehicle}) \\ &= 2.5 \times 10^{-3} \text{ g/s-m} \end{aligned}$$

Stability Class D applies for overcast conditions day or night regardless of wind speed as indicated in Table 10.3. Under Stability Class D, at $x=300\text{ m}$, $\sigma_z \approx 14\text{ m}$ from Figure 10.2. Substituting the appropriate input values from the problem statement, and as calculated earlier, into Equation 10.34 yields the following concentration for total hydrocarbons associated with this highway traffic:

$$c(300,0,0;0) = \frac{2(0.0025\text{ g/s-m})}{\sqrt{2\pi} (14\text{ m})(4\text{ m/s})} \exp\left[-\frac{1}{2}\left(\frac{0}{14\text{ m}}\right)^2\right] = \frac{0.005\text{ g/s-m}}{140.37\text{ m}^2/\text{s}}$$

$$= 3.56 \times 10^{-5} \text{ g Total HC/m}^3$$

Illustrative Example 10.12

A local nuclear utility has hired you to prepare an exposure assessment that is concerned with a potential radioactive release from a reactor. An earlier study indicated that for the release:

1. 1,000 of the 10,000 individuals located within 1 mile of the site will die.
2. 100 of the 100,000 individuals located between 1 and 5 miles of the plant will die.
3. 10 of the 1,000,000 individuals located between 5 and 20 miles of the facility will die.

Calculate the number of people exposed to the radioactive emission, as well as the number of people expected to die from the exposure.

Solution

The number of people exposed, NP , is

$$NP = 10,000 + 100,000 + 1,000,000 = 1,110,000$$

However, the number people who will die, PD , is

$$PD = 1000 + 100 + 10 = 1,110$$

This represents $1,110/1,110,000 = 0.001$ or 0.1% of the total population that will die from exposure to the radioactive release.

Illustrative Example 10.13

A nuclear power plant is located near the center of a medium-sized metropolitan area. Potential health concerns have surfaced regarding continuous radioactive emissions from the plant. "Toxicological" studies indicate that these concerns should be investigated and analyzed if

TABLE 10.5

Radioactive Field Measurements for Illustrative Example 10.13

Location (miles)	Population	Radioactive Concentration
<2	10,000	< c^*
2–5	200,000	> c^*
5–10	450,000	< c^*
>10	140,000	< c^*
Total	800,000	

the radioactive concentration(s) exceed a threshold value of c^* . Recently, radioactive field concentration measurements were obtained by Tonry Associates, and their results are provided in Table 10.5. Determine the number of individuals that are “exposed” to a potential radioactive problem.

Solution

From Table 10.5, 200,000 people are potentially exposed to radiation exceeding the threshold value of c^* at a distance of 2–5 miles around the plant. This represents $200,000/800,000 = 1/4$ or 25% of the total population in the metropolitan area and is a significant proportion of the area’s population, warranting future action and mitigation.

Illustrative Example 10.14

RAT (Ryan and Theodore) Associates have been requested to conduct an exposure assessment study at a chemical plant that is concerned with an incident involving a continuous 240 g/s release of ethylene oxide (EtO) at an elevation of 125 m. The wind speed is 9.0 miles/h and atmospheric Stability Class B applies. All individuals die if the concentration of the EtO is above $0.33 \mu\text{g/L}$; all individuals exposed to concentrations below this value are unaffected. The annual probability of the continuous emission occurring is 10^{-5} . A total of 50 people are located within the plant boundary. Ten people are located directly downwind of the discharge point; five are 350 m downwind and five are 600 m downwind near the plant fence line. All 10 individuals are at ground level.

RAT Associates have been specifically requested to calculate the number of individuals potentially affected within the plant boundary. *Hint:* Perform atmospheric dispersion calculations at various distances downwind from the emission point.

Solution

The dispersion calculations require determining the location(s) where the concentration of the chemical exceeds $0.33 \mu\text{g/L}$. First, assume a continuous emission for a point source. To maintain consistent units,

convert wind speed from miles/h to m/s and concentration from $\mu\text{g/L}$ to g/m^3 as follows:

$$u = (9.0 \text{ miles/h})(5280 \text{ ft/mile})(1 \text{ h}/3600 \text{ s})(0.3048 \text{ m/ft}) = 4.02 \text{ m/s}$$

$$c = (0.33 \mu\text{g/L})(1 \text{ g}/10^6 \mu\text{g})(10^3 \text{ L/m}^3) = 3.3 \times 10^{-4} \text{ g/m}^3$$

The atmospheric dispersion equation for the centerline, GLC with an elevated source given by Equation 10.26, is used with the input data provided in the problem statement to yield:

$$\begin{aligned} c(x, 0, 0; 125) &= \frac{q}{\pi\sigma_y\sigma_z u} \left\{ \exp \left[-\frac{1}{2} \left(\frac{H^*}{\sigma_z} \right)^2 \right] \right\} \\ &= \left(\frac{240 \text{ g/s}}{\pi(\sigma_y)(\sigma_z)(4.02 \text{ m/s})} \right) \exp \left[-\frac{1}{2} \left(\frac{125 \text{ m}}{\sigma_z} \right)^2 \right] \end{aligned}$$

where $c = 3.3 \times 10^{-4} \text{ g/m}^3$ at the critical point for adverse effects.

The downwind concentrations can be calculated based on the previous equation. The concentration results for select downwind distances are provided in Table 10.6. Results in Table 10.6 indicates that the maximum GLC is approximately $6.7 \times 10^{-4} \text{ g/m}^3$ and is located at a downwind distance of about 800 m. In addition, the “critical” zone is located between 500 and 1400 m.

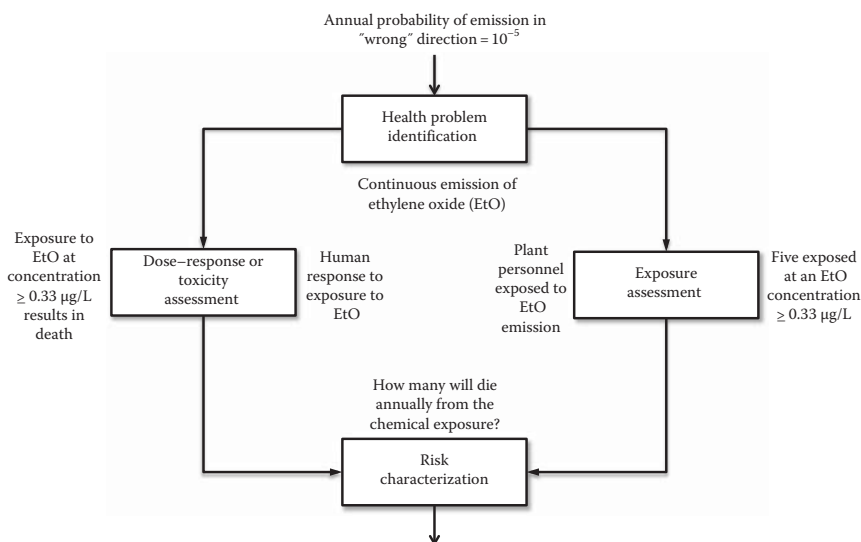
Based on the results provided in Table 10.6, one can determine which individuals downwind from the source will be killed. The five individuals located 600 m downwind of the emission source will die, while the five individuals located 350 m downwind are outside the critical zone will not die.

It should be noted that only one “average” weather condition was considered in this example. However, one often selects the worst-case weather condition that corresponds with a reasonable probability of occurrence in the location of the site being evaluated. Employing this

TABLE 10.6

Downwind Concentration Profile
for Illustrative Example 10.14

x (m)	σ_y (m)	σ_z (m)	c (g/m^3)
300	47	30	2.29×10^{-6}
500	75	52	2.71×10^{-4}
600	90	65	5.11×10^{-4}
800	120	90	6.71×10^{-4}
1000	170	140	5.36×10^{-4}
1500	250	240	2.77×10^{-4}
2000	300	380	1.58×10^{-4}

**FIGURE 10.4**

Plant HRA for Illustrative Example 10.14. See Illustrative Examples 11.17 and 11.18 for additional details.

worst-case condition produces risk results on the conservative side. An analysis that includes a full spectrum of wind speeds, directions, and stability classes would obviously provide a more thorough set of risk assessment calculations.

Illustrative Example 10.15

Refer to the previous example. Provide a HRA of this EtO release scenario using the framework shown in Figure 7.1.

Solution

The HRA of this EtO release problem is given in Figure 10.4. Note that the last step, i.e., risk characterization, cannot be completed at this time. Details of this step of the assessment are provided in the next chapter in Illustrative Examples 11.17 and 11.18.

10.5.3 Atmospheric Dispersion Equations for Instantaneous Sources

The previous section considered only sources that emit continuously. A rather significant amount of data and information are presented there. Unfortunately, little is available on instantaneous or "puff" source, a topic of interest in Part III. Turner's Workbook [7] provides an equation that may be used for estimation purposes for an instantaneous release of a hazardous contaminant in a HRA calculation. This approach is presented later.

The equations presented earlier apply only to sources emitting continuously or for periods equal to or greater than the travel times from the source to the point of interest. Cases of instantaneous releases, as from an explosion, or short-term releases on the order of seconds from tank or reactor venting episodes are also and often of practical concern. To determine concentrations at any position downwind resulting from these short-term releases, one must consider the time interval after the time of release, along with diffusion in the downwind direction as well as lateral and vertical diffusion considered for continuous releases. Of considerable importance, but very difficult to determine with certainty, is the path or trajectory of the “puff” as it moves away from the point of release. This is an important consideration if concentrations are to be determined at specific points downwind of the release. Determining the trajectory is of less importance if knowledge of the magnitude of the concentrations for particular downwind distances or travel times is required, but the exact points at which these concentrations occur need not be known. An equation that may be used for estimates of GLCs ($z=0$) downwind from an instantaneous release, t seconds after the release from an effective height, H^* , is [7]:

$$c(x,y,0; H^*) = \frac{2Q_T}{(2\pi)^{1.5}\sigma_x\sigma_y\sigma_z} \exp\left[-\frac{1}{2}\left(\frac{x-ut}{\sigma_x}\right)^2\right] \times \exp\left[-\frac{1}{2}\left(\frac{H^*}{\sigma_z}\right)^2\right] \exp\left[-\frac{1}{2}\left(\frac{y}{\sigma_y}\right)^2\right] \quad (10.37)$$

The notations have the usual meaning, with the important exceptions that Q_T represents the total mass of the release and the σ values are not those evaluated with respect to the dispersion of a continuous source at a fixed point in space. This equation can be simplified for centerline concentrations and ground level emissions by setting $y=0$ and $H^*=0$ to yield Equation 10.38:

$$c(x,0,0; 0) = \frac{2Q_T}{(2\pi)^{1.5}\sigma_x\sigma_y\sigma_z} \exp\left[-\frac{1}{2}\left(\frac{x-ut}{\sigma_x}\right)^2\right] \quad (10.38)$$

The σ values in Equations 10.37 and 10.38 refer to dispersion coefficients following the motion of the expanding puff. The σ_x value is the standard deviation of the concentration distribution in the puff in the downwind direction. Note that there is no dilution in the downwind direction by wind advection in Equations 10.37 and 10.38. The speed of the wind mainly serves to move the downwind position of the center of the puff, as shown by examination of the exponential term involving σ_x . Wind speed may influence the dispersion indirectly because the dispersion parameters σ_x , σ_y , and σ_z are functions of wind speed. The σ_y and σ_z values for an instantaneous source are less

TABLE 10.7

Estimation of Dispersion Parameters for
Quasi-Instantaneous Sources

Stability Condition	$x = 100 \text{ m}$		$x = 4 \text{ km}$	
	σ_y	σ_z	σ_y	σ_z
Unstable	10	15	300	220
Neutral	4	3.8	120	50
Very stable	1.3	0.75	35	7

Source: Turner, D., *Workbook of Atmospheric Dispersion Estimates*, rev., AP-26, U.S. EPA, Office of Air Programs, Research Triangle Park, NC, 1970.

than those for a continuous source given in Figures 10.2 and 10.3 but may be used as a first approximation. Others have suggested values for a σ_y and σ_z for quasi-instantaneous sources. These are given in Table 10.7. The problem remaining is to make best estimates of σ_x . Much less is known about the diffusion of a pollutant in the downwind direction than is known about lateral and vertical dispersion. In general, one should expect the σ_x value to be about the same value as σ_y [7].

Initial dimensions of the puff (e.g., from an explosion) may be approximated by finding a virtual distance similar to that for area sources to give the appropriate initial standard deviation for each direction. Then, σ_y will be determined as a function of $x + x_y$, σ_z as a function of $x + x_z$, and σ_x as a function of $x + x_z$.

Unless another model is available for treating instantaneous sources, it is recommended that Equations 10.37 and 10.38 be employed. The use of appropriate values of σ for this equation is not as clear-cut. As a first approximation, the reader may consider employing the values of σ provided in Table 10.7, with a σ_x value equal to that of σ_y . Quantifying the magnitude of the source term in Equation 10.37 is often a major challenge, and the reader is referred to work of NOAA and the EPA as embodied in the modeling package ALOHA (Aerial Locations of Hazardous Atmospheres) for more details on source term estimates and modeling approaches for instantaneous releases of hazardous materials from tanks, pipelines, reactors, pools, etc. [15,16].

Illustrative Example 10.16

A tank 30m high in a plant containing a toxic gas suddenly explodes, resulting in an emission of 200 g/s for 2 min. A school is located 500 m east and 100 m north of the plant. If this is an overcast day and the wind speed is 3.0 m/s from the west, how many seconds after the explosion will the concentration reach a maximum at the school? Humans will be adversely affected if the concentration of the gas is greater than 1.0 $\mu\text{g/L}$. Is there any impact on the students at the school?

Solution

For this problem the following input data should be used:

$$x = 500 \text{ m}, y = 100 \text{ m}, H^* = 30 \text{ m}, u = 4 \text{ m/s}$$

$$Q_T = (200 \text{ g/s})(2 \text{ min})(60 \text{ s/min}) = 24,000 \text{ g}$$

Stability Class D is applicable for overcast conditions. From Figures 10.2 and 10.3, approximate values (for $x=500\text{ m}$) are determined for the dispersion coefficients:

$$\sigma_y \approx 39 \text{ m}; \sigma_z \approx 19.5 \text{ m}$$

This is an approximately instantaneous source since the time for the plume to travel to the receptor point of interest, $t=x/u=500\text{ m}/(3\text{ m/s})=167\text{ s}$, is longer than the time of release of the chemical of 120 s. For an instantaneous release, Equation 10.37 applies, and the value of $\sigma_x \approx \sigma_y \approx 39 \text{ m}$. There is a maximum concentration at the school when the center of the plume reaches the school 500 m downwind from the release or when $t=167\text{ s}$.

Substitution of values given in the problem statement or calculated earlier into Equation 10.37 yields:

$$c(500,100,0;30) = \frac{2(24,000 \text{ g})}{(2\pi)^{1.5}(39\text{ m})(39\text{ m})(19.5\text{ m})} \exp \left[-\frac{1}{2} \left(\frac{500\text{ m} - 500\text{ m}}{39\text{ m}} \right)^2 \right] \\ \times \exp \left[-\frac{1}{2} \left(\frac{30\text{ m}}{19.5\text{ m}} \right)^2 \right] \exp \left[-\frac{1}{2} \left(\frac{100\text{ m}}{39\text{ m}} \right)^2 \right]$$

$$c(500,100,0;30) = \frac{2(24,000 \text{ g})}{(2\pi)^{1.5}(39\text{ m})(39\text{ m})(19.5\text{ m})} \exp \left[-\frac{1}{2} \left(\frac{30\text{ m}}{19.5\text{ m}} \right)^2 \right] \\ \times \exp \left[-\frac{1}{2} \left(\frac{100\text{ m}}{39\text{ m}} \right)^2 \right]$$

$$c(500,100,0;30) = (0.1028 \text{ g/m}^3)(0.306)(0.037) \\ = 0.00116 \text{ g/m}^3 = 1.16 \text{ }\mu\text{g/L}$$

Since this concentration is above the $1.0\text{ }\mu\text{g/L}$ adverse affect level for this chemical, children at the school exposed to this release will be adversely impacted. Hopefully, because of overcast conditions no children are

outside the building when the puff passes the school. Protection is provided inside the school from exposure to this elevated contaminant concentration, but because of the rapid travel time to the school, those children outside the building will likely suffer adverse affects if the warning to move indoors takes longer than 2 min.

Illustrative Example 10.17

A truck carrying two tanks containing a very unstable and hazardous gas is involved in an accident that results in the consecutive explosion of the tanks—one immediately, the second approximately 1 min later. The total mass of the emission resulting from the explosion of each tank is 30,000 g. The wind velocity is 1 m/s from the north, and the effective height of emission is 30 m at the time of the accident. Calculate the concentration of this gas 500 m south and 100 m east from the site 10 min after the explosion of the first tank. Assume that Stability Class D applies.

Solution

For this problem, the following input data should be used:

$$x = 500 \text{ m}, y = 100 \text{ m}, H^* = 30 \text{ m}, u = 1 \text{ m/s},$$

$$Q_T = 30,000 \text{ g (for each tank)}$$

Since Stability Class D is applicable, and since this can be modeled as an instantaneous source, Figures 10.2 and 10.3 yield the following values for the dispersion coefficients:

$$\sigma_y = \sigma_x = 39 \text{ m}; \sigma_z = 19.5 \text{ m}$$

Equation 10.37 again applies, and with substitution of values given earlier for the first tank, the concentration 10 min after the release at $t = 600 \text{ s}$, with $ut = (1 \text{ m/s})(600 \text{ s}) = 600 \text{ m}$, is:

$$c_1(500, 100, 0; 30) = \frac{2(30,000 \text{ g})}{(2\pi)^{1.5}(39 \text{ m})(39 \text{ m})(19.5 \text{ m})} \exp \left[-\frac{1}{2} \left(\frac{500 \text{ m} - 600 \text{ m}}{39 \text{ m}} \right)^2 \right] \\ \times \exp \left[-\frac{1}{2} \left(\frac{30 \text{ m}}{19.5 \text{ m}} \right)^2 \right] \exp \left[-\frac{1}{2} \left(\frac{100 \text{ m}}{39 \text{ m}} \right)^2 \right]$$

$$c_1(500, 100, 0; 30) = (0.128 \text{ g/m}^3) \exp \left[-\frac{1}{2} \left(\frac{-100 \text{ m}}{39 \text{ m}} \right)^2 \right] (0.306)(0.037)$$

$$c_1(500, 100, 0; 30) = 0.128 \text{ g/m}^3 (0.037)(0.306)(0.037) = 5.36 \times 10^{-5} \text{ g/m}^3$$

For the second tank that explodes 1 min later, its resultant plume has traveled for 9 min or 540 s, for a total travel distance = $ut = (1 \text{ m/s})(540 \text{ s}) = 540 \text{ m}$. Substituting the values given and calculated earlier for this second tank, the concentration it produces at the receptor is determined from Equation 10.37:

$$c_2(500, 100, 0; 30) = \frac{2(30,000 \text{ g})}{(2\pi)^{1.5}(39 \text{ m})(39 \text{ m})(19.5 \text{ m})} \exp \left[-\frac{1}{2} \left(\frac{500 - 540 \text{ m}}{39 \text{ m}} \right)^2 \right] \\ \times \exp \left[-\frac{1}{2} \left(\frac{30 \text{ m}}{19.5 \text{ m}} \right)^2 \right] \exp \left[-\frac{1}{2} \left(\frac{100 \text{ m}}{39 \text{ m}} \right)^2 \right]$$

$$c_2(500, 100, 0; 30) = (0.128 \text{ g/m}^3) \exp \left[-\frac{1}{2} \left(\frac{-40 \text{ m}}{39 \text{ m}} \right)^2 \right] (0.306)(0.037)$$

$$c_2(500, 100, 0; 30) = 0.128 \text{ g/m}^3 (0.591)(0.306)(0.037) = 8.56 \times 10^{-4} \text{ g/m}^3$$

Assuming that the concentrations are additive, the total concentration of the released gas at the receptor point, c_T , is:

$$c_T = c_1 + c_2 = 5.36 \times 10^{-5} \text{ g/m}^3 + 8.56 \times 10^{-4} \text{ g/m}^3 \\ = 9.09 \times 10^{-4} \text{ g/m}^3 = 909 \text{ } \mu\text{g/m}^3$$

Illustrative Example 10.18

Describe some of EPA's recent activities in improving predictive models of chemical exposure and resulting human health risk.

Solution

The EPA has recently developed a Stochastic Human Exposure and Dose Simulation (SHEDS) model to address exposure calculations associated with cumulative risk assessments. SHEDS can estimate the range of total chemical exposures in a population from different exposure pathways over different time periods, given a set of demographic characteristics. Calculations are based on available data on dietary consumption, human activity data drawn from EPA's Consolidated Human Activities Database, and measured chemical levels in food, water, and air plus concentrations measured on floors, counters, and walls. The model calculates an individual's sequential exposure to concentrations in different media and across multiple exposure pathways. The exposure estimates generated by the model are used as inputs to physiologically based pharmacokinetic models that predict how a chemical moves through and concentrates in human tissues and fluids, and how long it will take for the chemical to be naturally processed and excreted from the body.

Using SHEDS and these pharmacokinetic models provide a more accurate assessment of the risk certain chemicals pose to humans than previous modeling approaches. Extensive comparison of model results with real-world observations have shown that SHEDS/pharmacokinetic predictions agree very well with U.S. Centers for Disease Control and Prevention National Health and Nutrition Examination Survey results [17] and represents the future of exposure and risk assessment modeling.

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11

Health Risk Characterization

11.1 Introduction

Health risk characterization is the process of estimating the incidence of a health effect under the various conditions of human or animal exposure described in an exposure assessment. It is performed by combining the exposure assessment (see Chapter 10) with dose–response information (see Chapter 9). From a worker’s perspective, the risk from exposure to any chemical also depends on the potency associated with the effects and the duration of the exposure. The summary effects of the uncertainties in the preceding steps should also be included in this analysis.

The quantitative estimate of the risk is of principal interest to the regulatory agency or risk manager making a decision. The risk manager must consider the results of the risk characterization when evaluating the economics, societal aspects, and various benefits of the assessment. Factors such as societal pressure, technical uncertainties, and severity of the potential hazard influence how the decision makers respond to the risk assessment. As one might suppose, there is room for improvement in this step of the risk assessment [1,2].

A risk estimate indicates the likelihood of occurrence of the different types of health or environmental effects in exposed populations. Risk assessment should include both human health and environmental evaluations (e.g., impacts on ecosystems). Ecological impacts include actual and potential effects on plants and animals (other than domesticated species). The numbers produced from the risk characterization, representing the probability of adverse health effects being caused, must be evaluated.

Illustrative Example 11.1

Summarize the risk characterization step in a health risk assessment.

Solution

As noted earlier, risk characterization is the final step in the risk assessment process; it is the process of estimating a health effect under the various conditions described in the exposure assessment and is arrived

at by combining the results of the dose–response assessment with the exposure assessment. It should also describe the uncertainties encountered in each of these two steps and how they translate into uncertainties in the ultimate risk characterization. It is also important to identify questions and test the implicit or tacit assumptions that are often unknowingly made in the analysis.

Illustrative Example 11.2

Qualitatively describe the following terms:

1. Substantial risk
2. Unreasonable risk
3. Insignificant risk
4. *De minimis* risk
5. Acceptable risk

Solution

1. Each individual has a different concept of the meaning of the term *substantial* as it applies to health.
2. *Unreasonable* risk is an unacceptable risk, a risk level that is significantly (usually 1–2 orders of magnitude) above the EPA quantitative risk standard for lifetime probabilities of adverse effects.
3. The EPA has generally described *insignificant* risk quantitatively in terms of lifetime probabilities below which the risk is assumed low enough to be ignored.
4. *De minimis* risk is analogous to insignificant risk and has become a legal term that is decided on a case-by-case basis.
5. *Acceptable* risk generally suggests that the risk either is insignificant or perhaps zero.

This brief introduction section is followed by a host of topics related to health risk analysis and characterization. The subject matter includes:

Qualitative health risk scenarios
Quantitative risk: Noncarcinogens
Quantitative risk: Carcinogens
Risk uncertainties/limitations
Risk-based decision making
Public perception of risk

The reader should note that the general subject area in risk, uncertainties, and public perception are treated again in Part III. In effect, there is significant overlap when assessing health risk and hazard risk, particularly in the last three sections listed above.

11.2 Qualitative Health Risk Scenarios

Although the technical community has come a long way in understanding how to do a better job in the health problem identification, dose–response assessment, and exposure assessment portions of risk assessment, it has only begun to understand how to best characterize health risks and how to present these risks most appropriately to both the public and decision makers. The next three sections specifically address these issues. This section deals with qualitative risk assessment while the next two sections deal with quantitative risk assessment. This topic received superficial treatment in Chapter 7.

Regarding numerical values assigned to health risk, Paustenbach [1] provides the following comment:

Examination of the risks of common human activities demonstrates ... a lifetime risk of 1 in 100,000 or more is within the realm of, or orders of magnitude below, everyday risks that generally do not cause undue concern. These are risks that people, while they are aware of them and may have some concern or fear over them, do not in general alter their behavior to avoid ... the risks from many activities greatly exceed the level of 1 in 100,000. In comparison to these background risks of “everyday activities,” a lifetime risk of 1 in 100,000 is relatively small. Accordingly, regulatory action will not generally be justifiable unless risks are substantially higher than this 1 in 100,000 “benchmark.”

Numerous qualitative approaches to risk assessment have been employed. Some sample categorizations follow.

Qualitative health risk policies for companies, for example, Theodore and Dupont (TAD) Associates, could take the following forms:

1. TAD will not knowingly pose a greater risk to the public than it does to its own employees.
2. TAD will not expose its employees or neighbors to risks that are considered unacceptable based on industry practice and available technology.
3. TAD will comply with all applicable regulations and industry guidelines related to risks and will adopt its own standards where regulations do not exist or are inadequate.
4. TAD will neither undertake nor continue any operations whose associated risks it does not understand or cannot control at a safe level.

Another possible risk policy for a company could take the following form:

1. The average individual risk level for the public should be less than _____.
2. The maximum individual risk for TAD employees should be less than _____.
3. The probability of one or more public deaths should be less than _____.
4. The probability of 100 or more public deaths should be less than _____.
5. The probability of one or more public illnesses should be less than _____.
6. The probability of 100 or more public illnesses should be less than _____.

Once again, the aforementioned form can be applied on either an annual or lifetime basis.

The qualitative treatment of health risk assessment is also presented in Chapter 4 and in the Case Studies in Part IV. The qualitative treatment of hazard risk assessment can be found in Part III and in the Case Studies in Part IV.

Another qualitative (as well as quantitative) approach that may be employed involves the use of expert opinions. This method has been employed by one of the authors who has modestly referred to it as the Theodore panel approach (TPA). Most others refer to it as the Delphi panel approach (discussed superficially in Chapter 1). The Delphi panel approach has its origin based—there are numerous versions—on the oracle at Delphi in Greece (home of one of the author's ancestors). The city of Delphi became famous in ancient Greece because of Pythia, a priestess who muttered incomprehensible words (often with multiple meanings) that foretold the future. It is rumored that Alexander the Great violated the sacredness of Delphi by forcing Pythia to relent and provide the prophesy he desired.

At the simplest level, a group of experts are brought together to discuss a risk valuation in order to reach a consensus as to its most appropriate value. The procedure is iterative, with feedback between iterations, and involves five steps once the experts have been chosen. These five steps are as follows:

1. Select, in isolation, independent estimates of the risk *and* reasons/justification for the selected value.
2. Provide the initial results and reasons to the other experts.
3. Allow each expert to reverse his or her initial estimate and to provide the reasoning for any change to the initial value.

4. Repeat Steps 1 through 3 until a “consensus” value is approached.
5. Use the average of the final estimates as the best estimate of the risk.

In effect, the experts get locked in separate rooms, providing independent judgments, until some approach to convergence is achieved. Naturally, the experts (panelists) must be willing to share their knowledge, experience, and information with each other if this effort is to be successful.

Illustrative Example 11.3

Suggest a method for estimating the uncertainty associated with risk results generated using the TPA.

Solution

Use the standard deviation of the estimates as a measure of the uncertainty [3].

Illustrative Example 11.4

An incinerator burns mercury contaminated medical waste. The waste material has an ash content of 1%. The solid waste feed rate is 1,000 lb/h and the gas flow rate is 20,000 dscfm. The average mercury content of the particulate matter is 2.42 µg/g, while the vapor concentration is 0.3 mg/dscm. The incinerator meets the particulate standard of 0.08 g/dscf (0.1832 g/dscm) with a 99.5% efficient electrostatic precipitator (ESP). As part of a risk characterization study, calculate the amount of mercury (lb/day) bound to the fly ash that is captured in the ESP.

Solution

The amount of mercury bound to the fly ash that is captured in the ESP is calculated based on the mass of ash leaving the stack. This mass is calculated as follows:

Mass of ash out of stack

$$\begin{aligned}
 &= (0.08 \text{ g/dscf}) \left(\frac{1 \text{ lb}}{7000 \text{ g}} \right) (20,000 \text{ dscfm}) (60 \text{ min/h}) (24 \text{ h/day}) \\
 &= 329 \text{ lb ash/day}
 \end{aligned}$$

The mass exiting the stack represents 0.5% of the ash collected in the ESP, that is,

$$\text{Mass in the ESP} = \frac{329 \text{ lb/day}}{0.005} = 65,830 \text{ lb ash/day}$$

The daily amount of mercury bound to the fly ash in the ESP is calculated based on the mercury content of the fly ash:

Mercury in the ESP

$$\begin{aligned}
 &= (65,830 \text{ lb ash/day})(2.42 \times 10^{-6} \text{ g mercury/g ash}) (454 \text{ g/lb}) \\
 &= 72.3 \text{ lb/day}
 \end{aligned}$$

Illustrative Example 11.5

Medical sludge containing mercury is burned in an incinerator. The mercury feed rate is 9.2 lb/h. The resulting 500°F product (40,000 lb/h of gas; MW = 32 lb/lbmol) is quenched with water to a temperature of 150°F. The resulting stream is filtered to remove all particulates.

In an attempt to quantify the risk, the plant manager has asked: What happens to the mercury? Assume that the process pressure is 14.7 psi and that the vapor pressure of Hg at 150°F is 0.005 psi. The MW of mercury is 200.3 lb/lbmol.

Solution

For the mercury to be removed by the filter, it must condense and form particles. Therefore, the first question to be answered relates to the partial pressure of mercury during removal compared to its vapor pressure at 150°F:

Molar flow rate of Hg

$$= (9.2 \text{ lb/h}) / (200.6 \text{ lb Hg/lbmol}) = 0.046 \text{ lbmol/h}$$

Molar flow rate of gas

$$= (40,000 \text{ lb gas}) / (32 \text{ lb gas/lbmol}) = 1,250 \text{ lbmol/h}$$

The mole fraction of mercury may now be calculated:

$$y = \frac{\text{lbmol Hg}}{\text{lbmol Hg} + \text{lbmol gas}} = \frac{0.046 \text{ lbmol/h}}{0.046 \text{ lbmol/h} + 1250 \text{ lbmol/h}} = 3.68 \times 10^{-5}$$

The partial pressure is given by:

Partial pressure p_i

$$= y_i p = y_i (14.7 \text{ psia}) = 3.68 \times 10^{-5} (14.7 \text{ psia}) = 5.4 \times 10^{-4} \text{ psia}$$

Since the partial pressure of mercury in the quenched flue gas is much less than its vapor pressure at the quench temperature, mercury will NOT condense and thus will NOT be removed by the filter.

11.3 Quantitative Risk: Noncarcinogens

The EPA does not, at the present time, use a probabilistic approach to estimate the potential for noncarcinogenic health effects. Instead, the potential for noncarcinogenic effects is evaluated by comparing an exposure level over a specified time period (e.g., lifetime) with a reference dose derived for a similar exposure period. This ratio of exposure to toxicity is called a hazard quotient and is described below. (The reader is referred to Chapter 9 for additional details on the material that follows.) The noncancer hazard quotient assumes that there is a level of exposure (i.e., RfD) below which it is unlikely for even sensitive populations to experience adverse health effects and is expressed quantitatively as:

$$\text{Noncancer hazard quotient} = \frac{E}{RfD} \quad (11.1)$$

where

E is the exposure level (or intake)

RfD is the reference dose; E and RfD are expressed in the same units

If the exposure level exceeds this threshold (i.e., E/RfD exceeds unity), there may be concern for potential noncancer effects. As a rule, the greater the value of E/RfD above unity, the greater the level of concern. However, one should not interpret ratios of E/RfD as statistical probabilities; a ratio of 0.001 does not mean that there is a one in one thousand chance of the effect occurring. Further, it is important to emphasize that the level of concern does not increase linearly as the RfD is approached or exceeded because $RfDs$ do not have equal accuracy or precision and are not based on the same severity of toxic effects. Thus, the slopes of the dose–response curve in excess of the RfD can range widely depending on the substance.

Three exposure durations that will need separate consideration for the possibility of adverse noncarcinogenic health effects are chronic, subchronic, and shorter-term exposures. *Chronic* exposures for humans range in duration from 7 years to a lifetime; such long-term exposures are almost always of concern for Superfund sites (for inhabitants of nearby residences, year-round users of specified drinking water sources, etc.). *Subchronic* human exposures typically range in duration from 2 weeks to 7 years. For example, children might attend a junior high school near a Superfund site for no more than 2 or 3 years. Exposures less than 2 weeks in duration are occasionally of concern. Also, if chemicals known to be developmental toxicants are present at a site, *short-term* exposures of only a day or two can be of concern.

11.3.1 Risks for Multiple Substances

To assess the overall potential for noncarcinogenic effects posed by more than one chemical, a hazard index (HI) approach has been developed based on EPA's *Guidelines for Health Risk Assessment of Chemical Mixtures* [4]. This approach assumes that simultaneous subthreshold exposures to several chemicals could result in an adverse health effect. It also assumes that the magnitude of the adverse effect will be proportional to the sum of the ratios of the subthreshold exposures to acceptable exposures. The noncancer HI is equal to the sum of the hazard quotients, as described in Equation 11.2, where E and the RfD represent the same exposure period (e.g., subchronic, chronic, or shorter term):

$$HI = \frac{E_1}{RfD_1} + \frac{E_2}{RfD_2} + \cdots + \frac{E_i}{RfD_i} \quad (11.2)$$

where

E_i is the exposure level (or intake) for the i th toxicant

RfD_i is the reference dose for the i th toxicant; E and RfD are expressed in the same units

When the HI exceeds unity, there may be concern for potential health effects. While any single chemical with an exposure level greater than its toxicity value will cause the HI to exceed unity, the reader should note that for multiple chemical exposures, the HI can also exceed unity even if no single chemical exposure exceeds its RfD .

It is important to calculate the HI separately for chronic, subchronic, and short-term exposure periods as described below. It is also important to remember to include $RfDs$ for the noncancer effects of carcinogenic substances in a comprehensive health risk assessment.

11.3.2 Noncarcinogenic Effects: Chronic Exposures

For each chronic exposure pathway (i.e., 7 years to lifetime exposure), a separate chronic HI is calculated from the ratios of the chronic daily intake (CDI) to the chronic reference dose (RfD) for individual chemicals as described in the following equation:

$$\text{Chronic HI} = \frac{CDI_1}{RfD_1} + \frac{CDI_2}{RfD_2} + \cdots + \frac{CDI_i}{RfD_i} \quad (11.3)$$

where

CDI_i is the chronic daily intake for the i th toxicant in mg/kg-day

RfD_i is the chronic reference dose for the i th toxicant in mg/kg-day

11.3.3 Noncarcinogenic Effects: Subchronic Exposures

For each subchronic exposure pathway (i.e., 2 weeks to 7 year exposure), a separate subchronic HI is calculated from the ratios of subchronic daily intake (SDI) to the subchronic dose (RfDs) for individual chemicals as described in the following equation:

$$\text{Subchronic HI} = \frac{SDI_1}{RfDs_1} + \frac{SDI_2}{RfDs_2} + \cdots + \frac{SDI_i}{RfDs_i} \quad (11.4)$$

where

SDI_i is the subchronic daily intake for the i th toxicant, mg/kg-day

$RfDs_i$ is the subchronic reference dose for the i th toxicant, mg/kg-day

11.3.4 Noncarcinogenic Effects: Less than 2 Week Exposures

The same procedure may be applied for simultaneous shorter-term exposures to several chemicals. For drinking water exposures, 1 and 10 day Health Advisories can be used as reference toxicity values. Depending on available data, a separate HI might also be calculated for developmental toxicants (using RfD_{dt} s), which might cause adverse effects following exposures of only a few days.

There are several limitations to this approach that must be noted. As mentioned earlier, the level of concern does not increase linearly as the reference dose is approached or exceeded because the RfDs do not have equal accuracy or precision and are not based on the same severity of effects. Moreover, hazard quotients are combined for substances with RfDs based on critical effects of varying toxicological significance. RfDs of varying levels of confidence that include different uncertainty adjustments and modifying factors are also often combined (e.g., extrapolation from animals to humans, from lowest observed adverse effect levels (LOAELs) to no observed adverse effects levels (NOAELs), or from one exposure duration to another).

Another limitation to the HI approach is that the assumption of dose additivity is most properly applied to compounds that induce the same effect by the same mechanism of action. Consequently, the application of the HI equation to a number of compounds that are not expected to induce the same type of effects or that do not act by the same mechanism could overestimate the potential for effects, although such an approach is appropriate at a screening level. This possibility is generally not of concern if only one or two substances are responsible for driving the HI above unity.

If the HI is greater than unity as a consequence of summing several hazard quotients of similar value, it would be appropriate to segregate the compounds by effect and mechanism of action and to derive separate HIs for each group.

11.3.5 Segregation of Hazard Indices

Segregation of HIs by effect and mechanism of action can be complex and time consuming because it is necessary to identify all of the major effects and target organs for each chemical and then to classify the chemicals according to target organ(s) or mechanism of action. This analysis is not simple and should be performed by a toxicologist. If the segregation is not carefully performed, an underestimate of a true hazard could result. Agency review of particularly complex or controversial cases can be requested through the regional EPA risk assessment support staff.

The procedure for recalculating the HI by effect and by mechanism of action is briefly described later. If one of the effect-specific HIs exceeds unity, consideration of the mechanism of action might be warranted. A strong case is required, however, to indicate that two compounds that produce adverse effects on the same organ system (e.g., liver), although by different mechanisms, should not be treated as dose additive. Any such determination should be reviewed by a qualified toxicologist.

If there are specific data germane to the assumption of dose additivity (e.g., if two compounds are present at the same site and it is known that the combination is five times more toxic than the sum of the toxicities for the two compounds), then the development of the HI should be modified accordingly. The reader can refer to the EPA mixture guidelines for discussion of an HI equation that incorporates quantitative interaction data. If data on chemical interactions are available but are not adequate to support a quantitative assessment, one should note the information in the “assumptions” being documented for the risk assessment.

11.3.6 Combining Risks across Exposure Pathways

In some situations, an individual might be exposed to a substance or combination of substances through several pathways. For example, a single individual might be exposed to substance(s) from a hazardous waste site by consuming contaminated drinking water from a well, eating contaminated fish caught near the site, and through inhalation of dust originating from the site. The total exposure to various chemicals will equal the sum of the exposures by all pathways. However, one should not automatically sum risks from all exposure pathways evaluated for a site.

There are two steps required to determine whether risks or HIs for two or more pathways should be combined for a single exposed individual or group of individuals. The first is to identify reasonable exposure pathway combinations. The second is to examine whether it is likely that the same individuals would consistently face the “reasonable maximum exposure” (RME) by more than one pathway.

One should also identify exposure pathways that have the potential to expose the same individual or subpopulation at the key exposure areas

evaluated in the exposure assessment, making sure to consider areas of highest exposure for each pathway for both current and future land uses (e.g., nearest downgradient well and nearest downwind receptor). For each pathway, the risk estimates and HIs should be developed for a particular exposure area and time period; however, they do not necessarily apply to other locations or time periods. Hence, if two pathways do not affect the same individual or subpopulation, neither pathway's individual risk estimate or HI affects the other, and risks should not be combined.

Once reasonable exposure pathway combinations have been identified, it is necessary to examine whether it is likely that the same individuals would consistently face the RME. Note that the RME estimate for each exposure pathway includes many conservative and upper-bound parameter values and assumptions (e.g., upper 95th confidence limit on the amount of water ingested and upper-bound duration of occupancy of a single residence). Also, some of the exposure parameters are not predictable in either space or time (e.g., maximum downwind concentration may shift with wind direction and maximum groundwater plume concentration may move past a well). For real-world situations in which contaminant concentrations vary over time and space, the same individual may or may not experience the RME for more than one pathway over the same period of time. One individual might face the RME through a different pathway. The RME risks for more than one pathway can be combined *only* if one can explain why the key RME assumptions for more than one pathway should apply to the same individual or subpopulation.

In some situations, it may be appropriate to combine one pathway's RME risks with other pathway's risk estimates that have been derived from more typical exposure parameter values. In this way, resulting estimates of combined pathway risks may better relate to RME conditions.

If it is deemed appropriate to sum risks and HIs across pathways, the risk assessor should clearly identify those exposure pathway combinations for which a total risk estimate or HI is being developed. The rationale supporting such combinations should also be clearly stated.

To assess the overall potential for noncarcinogenic effects posed by several exposure pathways, the total HI for each exposure duration (i.e., chronic, subchronic, and shorter term) should be calculated separately. This approach is described in the following equation:

$$\begin{aligned} &\text{Total exposure hazard index (TEHI)} \\ &= \text{Hazard index (exposure pathway}_1\text{)} + \text{Hazard index} \\ &\quad \times (\text{exposure pathway}_2\text{)} + \cdots + \text{Hazard index (exposure pathway}_i\text{)} \quad (11.5) \end{aligned}$$

Note that the TEHI should be calculated separately for chronic, subchronic, and shorter-term exposure periods.

When the total HI for an exposed individual or group of individuals exceeds unity, there may be concern for potential noncancer health effects. As indicated before, for multiple exposure pathways, the HI can exceed unity even if no single exposure pathway HI exceeds unity. If the total HI exceeds unity and if combining exposure pathways has resulted in combining HIs based on different chemicals, one may need to consider segregating the contributions of the different chemicals according to their major effect and reevaluate the overall risk posed to the exposed population at the site.

Illustrative Example 11.6

List the possible sources of highly toxic hexavalent chromium (Cr^{6+}) and methods to reduce risks from exposure to it by removing it from a wastewater stream.

Solution

Hexavalent chromium-bearing wastewater is produced in chromium electroplating, chromium conversion coating, etching with chromic acid, and metal-finishing operations carried out using chromium as the base material.

Chromium wastes are commonly treated in a two-stage batch process. The primary stage is used to reduce the highly toxic hexavalent chromium to the less toxic trivalent chromium. There are several ways to reduce the hexavalent chrome to trivalent chrome including the use of sulfur dioxide, bisulfite, or ferrous sulfate. The trivalent chrome is then removed by hydroxide precipitation. Most processes use caustic soda (NaOH) to precipitate chromium hydroxide. Hydrated lime [$\text{Ca}(\text{OH})_2$] may also be used in this precipitation step.

Illustrative Example 11.7

Xylene is one of the organic compounds found in gasoline, and high vapor concentrations have been measured in ambient at gasoline stations. If the yearly average concentration of xylene at a neighborhood gas station in California is $220\mu\text{g}/\text{m}^3$, what is the HI associated with long-term exposure? Likewise, if the peak 1 h average concentration near the pumps is $1000\mu\text{g}/\text{m}^3$, what is the HI for short-term (acute) exposure? *Note:* The chronic and acute reference exposure limits (RELs) for xylene are $300\mu\text{g}/\text{m}^3$ and $4400\mu\text{g}/\text{m}^3$, respectively.

Solution

To determine a chronic noncarcinogenic risk, the 1 year average concentration is used as the chronic exposure level, along with the chronic REL for the exposure dose in Equation 11.1. If the pollutant causes an acute noncarcinogenic risk, the maximum 1 h concentration is used for the exposure level, and the acute REL is used for the reference dose. In this procedure, an HI is calculated for each pollutant separately, and then the

indices are summed for each toxicological end point (i.e., the respiratory system, the central nervous system, etc.). Finally, the total HI is then compared to a value that is considered significant.

To assess the noncarcinogenic risks associated with this xylene exposure, Equation 11.1 is used, with E representing the xylene concentration in units of $\mu\text{g}/\text{m}^3$, and RfD , the reference exposure level, in $\mu\text{g}/\text{m}^3$ for the chronic or short-term exposure scenario being considered.

Applying a modified form of Equation 11.1, the HI for chronic exposure to xylene concentrations at the gas station is:

$$\text{Chronic HI} = \frac{\text{Yearly average concentration}}{\text{Chronic REL}} = \frac{220\mu\text{g} / \text{m}^3}{300\mu\text{g} / \text{m}^3} = 0.73$$

The HI for acute exposure to the emissions near the pumps is:

$$\text{Acute HI} = \frac{\text{1h average concentration}}{\text{Acute REL}} = \frac{1000\mu\text{g} / \text{m}^3}{4400\mu\text{g} / \text{m}^3} = 0.23$$

In California, an HI greater than 0.5 is considered to be significant. Therefore, if xylene was the only contaminant at the gas station, the long-term exposure could be considered hazardous, while the short-term exposure to the emissions near the pump would not.

11.4 Quantitative Risk: Carcinogens

For carcinogens, risks are estimated as the incremental probability of an individual developing cancer over a lifetime as a result of exposure to the potential carcinogen (i.e., incremental or excess individual lifetime cancer risk). The guidelines provided in this section are consistent with EPA's *Guidelines for Carcinogen Risk Assessment* [5]. For some carcinogens, there may be sufficient information on mechanism of action that a modification of the approach outlined in the following is warranted. Once again, the reader is referred to Chapter 9 for additional details on the material presented below.

The slope factor (SF) converts estimated daily intakes, averaged over a lifetime of exposure, directly to incremental risk of an individual developing cancer. Because relatively low intakes (compared to those experienced by test animals) are most likely from environmental exposures at most sites, it is generally assumed that the dose-response relationship will be linear in the low-dose portion of the multistage model dose-response curve. Under this assumption, the SF is a constant, and risk will be directly related to intake. This linear low-dose risk equation is described in the following:

$$\text{Risk}_{LD} = (CDI)(CSF) \quad (11.6)$$

where

$Risk_{LD}$ is a unitless probability (e.g., 2×10^{-5}) of an individual developing cancer at low-dose conditions

CDI is the chronic daily intake averaged over 70 years, mg/kg-day

CSF is the carcinogenic SF, expressed in (mg/kg-day) $^{-1}$

The risk obtained from Equation 11.6 may be viewed as the product of an exposure term (CDI) and a cancer “potency” factor, SF. However, this linear equation is valid only at low risk levels (i.e., below estimated risks of 0.01). For situations where chemical intakes might be high (i.e., risk above 0.01), an alternate equation should be used. The *one-hit* equation, which is consistent with the linear low-dose model given above and described in the following equation, should be used instead:

$$Risk_{HD} = 1 - e^{-(CDI \times SF)} \quad (11.7)$$

where $Risk_{HD}$ is a unitless probability (e.g., 2×10^{-5}) of an individual developing cancer at high dose levels.

Because the SF is often an upper 95% confidence limit of the probability of response based on experimental animal data used in the multistage model, the carcinogenic risk estimate will generally be an upper-bound estimate. This means that the EPA is reasonably confident that the “true risk” will not exceed the risk estimate derived through use of this model and is likely to be less than that predicted.

11.4.1 Risks for Multiple Substances

The cancer risk equation described in this section estimates the incremental individual lifetime cancer risk for simultaneous exposure to several carcinogens and is based on EPA's *Risk Assessment Guidelines for Carcinogens* [4]. This equation represents an approximation of the “precise” equation for combining risks that accounts for the joint probabilities of the same individual developing cancer as a consequence of exposure to two or more carcinogens. The difference between the precise equation and the approximation described earlier is negligible for total cancer risks less than 0.1. Thus, the simple additive equation is appropriate for most risk assessments. The cancer risk equation for multiple substances is then given by:

$$Risk_T = \sum Risk_i = \sum R_i \quad (11.8)$$

where

$Risk_T$ is the total cancer risk

$Risk_i = R_i$ is the risk estimate for the i th substance, both expressed as a unitless probability

The risk summation technique assumes that the intake of individual substances is small. It also assumes independence of action by the compounds involved (i.e., there are no synergistic or antagonistic chemical interactions and that all chemicals produce the same effect, i.e., cancer). If these assumptions are incorrect, over- or underestimation of the actual multiple-substance risk could result.

There are several limitations to this approach that must be noted. First, because each SF is an upper 95th percentile estimate of potency and because upper 95th percentiles of probability distributions are not strictly additive, the total cancer risk estimate might become artificially more conservative as risks from a number of different carcinogens are summed. If one or two carcinogens drive the risk, however, this problem is of reduced concern. Second, it will often be the case that substances with different weights of evidence for human carcinogenicity are included. The cancer risk equation for multiple substances adds all carcinogens equally. In addition, SFs derived from animal data will be given the same weight as SFs derived from human data. Finally, the action of two different carcinogens might not be independent.

11.4.2 Combining Risk across Exposure Pathways

The reader should note that the introductory comments in Section 11.3.6 apply to carcinogens as well. The calculation proceeds as follows. First, sum the cancer risks for each exposure pathway contributing to the exposure of the same individual or subpopulation. For Superfund risk assessments, cancer risks from various exposure pathways are assumed to be additive as long as the risks are for the same individuals and time period (i.e., less-than-lifetime exposures have all been converted to equivalent lifetime exposures). This summation procedure is described as:

$$\begin{aligned} &\text{Total exposure cancer risk} \\ &= \text{Risk (exposure pathway}_1) + \text{Risk (exposure pathway}_2) \\ &\quad + \cdots + \text{Risk (exposure pathway}_i) \end{aligned} \tag{11.9}$$

Although the exact equation for combining risk probabilities includes terms for joint risks, the difference between the precise equation and the approximation presented in Equation 11.9 is negligible for total cancer risks of less than 0.1.

Illustrative Example 11.8

At the maximum allowable EPA level of 5 parts per billion (ppb) PCE (tetrachloroethylene), a person would have to drink 2 L of water per day for 70 years to increase the risk of getting cancer by 1 in 10,000. If one

drinks 2 L of water per day for 70 years, what is the increased risk of getting cancer when the concentration of PCE in water is 0.01 parts per million (ppm)?

Solution

As stated earlier, the chance of getting cancer by drinking 2 L of water per day for 70 years that contains 5 ppb of PCE is 1/10,000. (This probability is the same as 0.0001). To convert 0.01 ppm to ppb:

$$0.01 \text{ ppm} \left(\frac{1000 \text{ ppb}}{1 \text{ ppm}} \right) = 10 \text{ ppb}$$

The ratio of the actual exposure concentration to the 5 ppb standard is used to determine the relative risk of this actual exposure or:

$$\left(\frac{10 \text{ ppb}}{5 \text{ ppb}} \right) (0.0001 \text{ risk}) = 2 (0.0001) = 0.0002 = \frac{2}{10,000} \text{ or } \frac{1}{5,000}$$

Therefore, the risk is twice as great, i.e., 1 in 5000.

Illustrative Example 11.9

Several industrial facilities near a residential area emit the inhalable pollutants ethylene oxide (EtO), polychlorobiphenyls (PCBs), and polycyclic aromatic hydrocarbons (PAHs). The annual average concentration of EtO, PCBs, and PAHs are 10, 2, and 5 $\mu\text{g}/\text{m}^3$, respectively.

Calculate the cancer risk caused by each pollutant and the total cancer risk. Express the results in additional cancer cases per million people. The cancer risk caused by each hazardous chemical can be calculated using Equation 11.10 (a modified form of Equation 11.6) and data presented in Table 11.1:

$$\text{Cancer risk} = (\text{Average concentration})(\text{Unit cancer risk}) \quad (11.10)$$

Solution

Applying Equation 11.10 yields:

TABLE 11.1

Data for Illustrative Example 11.9

Pollutant	Unit Risk ($\text{m}^3/\mu\text{g}$)
EtO	8.8×10^{-5}
PCBs	1.4×10^{-3}
PAHs	1.7×10^{-3}

Cancer risk of ethylene oxide

$$\begin{aligned} &= (10 \mu\text{g}/\text{m}^3)(8.8 \times 10^{-5} \text{m}^3/\mu\text{g}) = 88 \times 10^{-5} = 880 \times 10^{-6} \\ &= 880 \text{ excess cancer cases per million people} \end{aligned}$$

The cancer risk caused by PCBs is estimated to be:

Cancer risk of PCBs

$$\begin{aligned} &= (2 \mu\text{g}/\text{m}^3)(1.4 \times 10^{-3} \text{m}^3/\mu\text{g}) = 2.8 \times 10^{-3} = 2800 \times 10^{-6} \\ &= 2,800 \text{ excess cancer cases per million people} \end{aligned}$$

The cancer risk caused by PAHs is estimated to be:

Cancer risk of PAHs

$$\begin{aligned} &= (5 \mu\text{g}/\text{m}^3)(1.7 \times 10^{-3} \text{m}^3/\mu\text{g}) = 8.5 \times 10^{-3} = 8500 \times 10^{-6} \\ &= 8,500 \text{ excess cancer cases per million people} \end{aligned}$$

The total cancer risk by inhalation is calculated from the arithmetic sum of individual cancer risks, assuming no interaction of pollutants in terms of carcinogenic effects:

$$\begin{aligned} \text{Total cancer risk} &= 880 + 2,800 + 8,500 \\ &= 12,180 \text{ excess cancer cases per million people} \end{aligned}$$

The rate is extremely high, since it is 12,180 times higher than the 1 in a million cancer risk normally used as a basis for management of air toxics. This situation should be rectified as soon as possible by a reduction in these three air toxics. Also note that the PAHs contribute the majority of risk at this facility, and should be the primary target of risk reduction efforts.

Illustrative Example 11.10

Environmental tobacco smoke (ETS) and gasoline vapors both contain mixtures of trace amounts of many of the individual compounds regulated as Air Toxics under Title III, Section 112 of the 1990 Clean Air Act Amendments. Much of the general public is more likely to be exposed to these mixtures during the course of their lives than to specific compounds on the air toxics list. Hence, the estimation of the cancer risk resulting from exposure to these mixtures is a useful and relevant exercise.

Which of the following mixtures of air toxics imposes the greatest cancer risk to an individual breathing it for 70 years at an average concentration of $5 \mu\text{g}/\text{m}^3$? The following unit cancer risk values were obtained from Ref. [6]:

1. ETS [unit cancer risk $2.80 \times 10^{-5} (\mu\text{g}/\text{m}^3)^{-1}$]
2. Gasoline vapors [unit cancer risk $1.60 \times 10^{-6} (\mu\text{g}/\text{m}^3)^{-1}$]

Solution

To solve this problem, compute the cancer risk for each air toxic mixture by multiplying the average concentration by the unit cancer risk.

1. For ETS,

$$\begin{aligned}\text{Risk} &= (5 \mu\text{g}/\text{m}^3)(2.80 \times 10^{-5}) \\ &= 1.40 \times 10^{-4} = 140 \text{ in } 10^6 \text{ (140 in a million)}\end{aligned}$$

2. For gasoline vapors,

$$\begin{aligned}\text{Risk} &= (5 \mu\text{g}/\text{m}^3)(1.60 \times 10^{-5}) \\ &= 8.00 \times 10^{-5} = 80 \text{ in } 10^6 \text{ (80 in a million)}\end{aligned}$$

Since 140 in 10^6 exceeds 80 in 10^6 , the conclusion is that for identical durations of exposure to identical concentrations in air, ETS poses nearly twice the cancer risk of gasoline vapors. However, both mixtures exhibit high cancer risks at trace levels as observed from these calculations.

Illustrative Example 11.11

A groundwater plume has developed from a leaking underground storage tank (LUST) and fumes have migrated to the basement of nearby homes. A sample of indoor air indicates toluene and benzene concentrations of 50 and $70 \mu\text{g}/\text{m}^3$, respectively. Determine the resulting health risk for a 70 kg adult living in the residence who is exposed to these vapors for 15 years, assuming a breathing rate of $15 \text{ m}^3/\text{day}$ and 75% absorption of both toluene and benzene. The carcinogenic SF risk-specific doses (RSDs) via the inhalation route are 0.021 and $0.028 (\text{mg}/\text{kg}\cdot\text{day})^{-1}$ for toluene and benzene, respectively. Assume the environmental health risks for toluene and benzene are additive. To calculate the environmental risk, Equation 11.11 can be used as follows:

$$\text{RISK} = \frac{(C)(CSF)(BR)(DUR)}{(ABW)(LIFE)} \quad (11.11)$$

where

$RISK$ is the probability of cancer, dimensionless

C is the air concentration, mg/m^3

CSF is the carcinogenic SF, $\text{RSDs} (\text{mg}/\text{kg}\cdot\text{day})^{-1}$

BR is the breathing rate, m^3/day

DUR is the exposure duration period, year

ABW is the average body weight, kg

$LIFE$ is the lifetime exposure of 70 years

Note: The RSD is an estimate of the average daily dose of a carcinogen that corresponds to a specific excess cancer risk for a 70 year lifetime exposure.

Solution

Based on the problem statement, apply Equation 11.8:

$$\text{Total risk} = RISK_{\text{toluene}} + RISK_{\text{benzene}}$$

Using Equation 11.11, the environmental risks of toluene and benzene are determined as follows:

$$\begin{aligned} RISK_{\text{toluene}} &= \frac{(50 \text{ mg}/\text{m}^3)(0.021 \text{ kg}\cdot\text{day}/\text{mg})(15 \text{ m}^3/\text{day})(15 \text{ year})}{(70 \text{ kg})(70 \text{ year})} \\ &\times \frac{(1 \text{ kg})}{(1000 \text{ mg})} = 4.82 \times 10^{-5} \end{aligned}$$

$$\begin{aligned} RISK_{\text{benzene}} &= \frac{(70 \text{ mg}/\text{m}^3)(0.028 \text{ kg}\cdot\text{day}/\text{mg})(15 \text{ m}^3/\text{day})(15 \text{ year})}{(70 \text{ kg})(70 \text{ year})} \\ &\times \frac{(1 \text{ kg})}{(1000 \text{ mg})} = 9.0 \times 10^{-5} \end{aligned}$$

$$\begin{aligned} \text{Total risk} &= RISK_{\text{toluene}} + RISK_{\text{benzene}} \\ &= 4.82 \times 10^{-5} + 9.0 \times 10^{-5} = 1.38 \times 10^{-4} \end{aligned}$$

Under these conditions, one could expect 1.38 additional cases of cancer per 10,000 or 138 additional cases of cancer per 1,000,000 people exposed to toluene and benzene from this source over their lifetime.

11.5 Risk Uncertainties/Limitations

Although great controversy can surround results of risk assessments, especially quantitative risk assessments, they are useful in particular applications.

They can help establish priorities for regulatory action or interventions of any type. A uniform risk assessment performed across a range of substances can create a spectrum of their health risks to humans. The limits of risk assessment can also be tested when government agencies (faced with the absence of other types of data and the need for action) must rely on risk assessment methods to establish health-based standards or guidelines to prevent human exposure to hazardous substances. Because of risk assessment shortcomings and the desire for greater specificity in measuring exposure, increasing interest is being shown in understanding pathologic changes at the molecular level with the hope that these investigations will permit toxicological and epidemiological analyses of greater accuracy and sensitivity than are currently available (see Chapter 9) [7,8]. In a general sense, problems in this area arise because of:

1. Uncertainty associated with available data
2. Concerns associated with assumed information
3. Uncertainty associated with governing equations
4. Concerns associated with limited and/or constrained governing equations
5. Concerns associated with overall analysis quality

11.5.1 Uncertainty and Variability

In the risk characterization step of a human health risk assessment, conclusions about hazard and dose response are integrated with those from the exposure assessment step. In addition, confidence about these conclusions, including information about the uncertainties associated with each aspect of the assessment in the final risk summary, should be highlighted. In the previous assessment steps and in the risk characterization, the risk assessor should also distinguish between variability and uncertainty.

Variability arises from true heterogeneity in characteristics such as dose-response differences within a population or differences in contaminant levels in the environment. The values of some variables used in an assessment change with time and space or across the population whose exposure is being estimated. Assessments should address the resulting variability in doses received by members of the target population. Individual exposure, dose, and risk can vary widely in a large population. The central tendency and high-end individual risk descriptors are intended to capture the variability in exposure, lifestyles, and other factors that lead to a distribution of risk across a population.

Uncertainty, on the other hand, represents lack of knowledge about factors such as adverse effects or contaminant levels, which may be reduced with additional study. Generally, risk assessments involve several categories of uncertainty, and each merits consideration. Measurement uncertainty refers

to the usual error that accompanies scientific measurements—standard statistical techniques applied to analytical quality control data [3] can often be used to express measurement uncertainty. A substantial amount of uncertainty is often inherent in environmental sampling, and assessments should also address these uncertainties. Likewise, there are uncertainties associated with the use of scientific models, e.g., dose–response models, and models of environmental fate and transport. Evaluation of model uncertainty should consider the scientific basis for the model and their available empirical validation.

Another measure of uncertainty is the agreement technical risk assessment personnel might have regarding their ranking of the relative risk a range of environmental problems might represent to the general public. Such an evaluation of relative risk ranking was undertaken by EPA [9] with some interesting results. Some of the working groups EPA asked to consider relative risk had difficulty ranking 31 environmental problem issues they were presented with because there are no accepted guidelines for quantitatively assessing relative risks. As noted in the EPA's study, the following general results were produced for each of four types of risks (cancer health risk, noncancer health risk, ecological risk, and welfare risk) these working groups considered:

1. No problems rank high or relatively low in all four types of risk
2. Problems that rank relatively high in three of the four types, or at least medium in all four, include criteria air pollutants, stratospheric ozone depletion, pesticide residue on food, and other pesticide risks (runoff and air deposition of pesticides)
3. Problems that rank relatively high in cancer and noncancer health risks but low in ecological and welfare risks include hazardous air pollutants, indoor radon, indoor air pollution other than radon, pesticide application, exposure to consumer products, and worker exposures to chemicals
4. Problems that rank relatively high in ecological and welfare risk but low in both health risks include global warming, point and nonpoint sources of surface water pollution, physical alteration of aquatic habitats (including estuaries and wetlands), and mining waste
5. Areas related to groundwater consistently rank medium or low in the four risk categories

Although there were great uncertainties involved in making these assessments, the divergence between the EPA's programmatic efforts and relative risks is noteworthy. From this study, areas of relative high risk but low EPA program effort include indoor radon, indoor air pollution, stratospheric ozone depletion, global warming, nonpoint sources, discharges to estuaries, coastal waters and oceans, other pesticide risks, accidental releases of toxics, consumer products, and worker exposures. EPA

programs, on the other hand, give high priority to relatively medium- to low-risk environmental problems (as identified by working group experts) that include RCRA sites, Superfund sites, USTs, and municipal nonhazardous waste sites.

It should be noted that there is no completely satisfactory way to generate accurate risk data since it is an inexact science fraught with uncertainties. At a minimum, risk characterization should be checked against experience for reasonableness since the size and quality of the data employed does not permit an accurate quantitative estimate with a high degree of confidence. Careful documentation of all four parts of a risk assessment should also be maintained to prevent the practitioner from falling into traps that can influence the final results or pass the risk via a cross-media process on to another location or vulnerable population. Finally, EPA and OSHA have compounded the human health risk assessment uncertainty problem because of some of their ambiguous and conflicting rules and regulations.

11.5.2 Assessment and Presentation of Uncertainty

The risk measures used, for example, in Superfund site risk assessments usually are not fully probabilistic estimates of risk, but conditional estimates given a considerable number of assumptions about exposure and toxicity (e.g., risk given a particular future land use). Thus, it is important to fully specify the assumptions and uncertainties inherent in risk assessments to place the risk estimates in proper perspective. Another use of uncertainty characterization can be to identify areas where a moderate amount of additional data collection might significantly improve the basis for selection of a remedial alternative or risk mitigation effort.

Highly quantitative statistical uncertainty analysis is usually not practical or necessary for human health risk assessments for a number of reasons, not the least of which are the resource requirements to collect and analyze scenario data in such a way that the results can be presented as valid probability distributions. As in all environmental risk assessments, it is already known that uncertainty about the numerical results is generally large (i.e., on the range of at least an order of magnitude or greater). Consequently, it is more important to identify the key scenario-related variables and assumptions that contribute most to the uncertainty than to precisely quantify the degree of uncertainty in the risk assessment.

There are several categories of uncertainties associated with human health risk assessments. One is the initial selection of substances used to characterize exposures and risk on the basis of sampling data and available toxicity information. Other sources of uncertainty are inherent in the toxicity values for each substance used to characterize risk. Additional uncertainties are inherent in the exposure assessment for individual substances and individual exposures. These uncertainties are usually driven by uncertainty in the chemical monitoring data and the models used to estimate exposure

concentrations in the absence of monitoring data, but can also be driven by population intake parameters. As described earlier, additional uncertainties are incorporated in the risk assessment when exposures to several substances across multiple pathways are summed.

Once risk estimates with accompanying uncertainties have been ascertained, strategies are implemented to control/reduce these risks. The usual procedure involves the application of a cost-benefit analysis where calculations are performed to determine the processes/conditions for realizing the maximum benefits and/or minimum impacts to the exposed population. For alternate strategies, the one yielding the maximum benefit is, subject to constraints in the analysis, the optimum one chosen for implementation.

Illustrative Example 11.12

Discuss health problems with delayed effects and their impact on risk estimates.

Solution

The cause of the health problem may not be obvious if a health problem effect is delayed. This applies to many chronic diseases. The question of causality is important for this class of risk. The delayed effect obviously increases the uncertainties associated with any risk estimate.

11.6 Risk-Based Decision Making

A variety of EPA programs involved in the protection of groundwater and cleanup of environmental contamination utilize a risk-based decision making approach. The use of a risk-based decision-making process allows for efficient allocation of limited resources, such as time, money, regulatory oversight, and/or qualified professionals. Advantages of using this process include the following:

1. Decisions are based on reducing the risk of adverse human or environmental impacts.
2. Site assessment activities are focused on collecting only that information that is necessary to make risk-based corrective action decisions.
3. Limited resources are focused on those sites that pose the greatest risk to human health and the environment at any time.
4. Compliance can be evaluated relative to site-specific standards applied at site-specific point(s) of compliance.

5. Higher quality, and in some cases, faster cleanups may be achieved than are currently possible.
6. Documentation is developed that can demonstrate that the remedial action is protective of human health, safety, and the environment.

By using risk-based decision making, decisions are thus made in a consistent manner. Protection of both human health and the environment can be accounted for in most cases [10].

Under the EPA's regulations dealing with cleanup of UST sites, regulators are expected to establish cleanup goals for UST releases based on consideration of factors that could influence human and environmental exposure to contamination. Where UST releases affect groundwater being used as public or private drinking water sources, the EPA generally recommends that cleanup goals be based on health-based drinking water standards. Even in such cases, however, risk-based decision making can be employed to focus the implementation of corrective action efforts [10]. The reader should note that the bulk of this material also applies to hazard risk assessment, a topic that is treated in Part III.

Risk-based decision making and risk-based corrective action (RBCA) are decision making processes for assessing and responding to a health hazard. The processes take into account effects on human health and the environment, inasmuch as chemical releases vary greatly in terms of complexity, physical, and chemical characteristics, and in the risk that they may pose. RBCA was initially developed by the American Society for Testing and Materials (ASTM) [11] to assess petroleum releases, but the process may be tailored for use with any hazard.

The EPA and several state environmental agencies have developed similar decision-making tools. The EPA refers to the process as "risk-based decision making." While the ASTM RBCA standard deals exclusively with human health risk, the EPA advises that, in some cases, ecological impacts must also be considered in establishing cleanup goals [10].

11.7 Public Perception of Risk

Public concern about risk ranges from toxins in food and water, earthquakes, fires, and hurricanes to asbestos, radon emissions, ozone depletion, etc. Many of the public's worries are out of proportion because the fear is either overestimated or at times underestimated. The risks given the most publicity and attention tend to receive the greatest concern, while the ones that are more familiar and accepted are given less thought.

A large part of what the public knows about risk comes from the media. Whether it is newspapers, magazines, radio, or television, the media provides

information about the nature and extent of specific risks. The media also helps shape the perception of the danger involved with a given risk.

Laypeople and experts disagree on risk estimates for many environmental problems. This creates a problem, since the public generally does not trust the experts. This section concentrates on how the public views risk and what the future of public risk perception may be. The reader should note that much of this material, as with the previous section, applies to hazard risk assessment—a topic that is treated in Part III.

11.7.1 Everyday Risks

The public often worries about the largely publicized risks and thinks little about those that they face regularly. A consensus ranking from risk assessment experts of environmental problem areas based on overall population cancer risk [9] is summarized in Table 11.2. This ranking identifies indoor radon exposure, indoor air pollution exposure, and chemical exposure via consumer product use as three of the top five environmental problem areas facing the general population. This summary, along with results of a study reported on in 1985 [12–14] that compared the responses of two groups, 15 national risk assessment experts and 40 members of the League of Women Voters, highlights the discrepancy between risk perception by risk experts versus the general public. In the 1985 study, when asked to rank the risks of 30 activities and technologies (see Table 11.3), the League members rated nuclear power as the number 1 risk, while risk experts numbered it at 20, and the League ranked x-rays at 22, while the experts gave it a rank of 7. This topic and this specific study will be discussed in Illustrative Example 12.15.

There are various reasons for the differences in risk perception between the public and technical experts. Government regulators and industry officials look at different aspects when assessing a given risk than would members of a community, and members of a community often have risk perceptions affected by *outrage factors*.

11.7.2 Outrage Factors

The perception of a given risk is amplified by what are known as “outrage” factors. These factors can make people feel that even small risks are unacceptable. More than 10 outrage factors were first identified by Sandman [15], and a few of the main ones are defined in the following [16]:

1. *Voluntariness*. A voluntary risk is much more acceptable to people than an imposed risk. People will accept the risk from skiing, but not from food preservatives, although the potential for injury from skiing is 1000 times greater than from preservatives.
2. *Control*. Risks that people can take steps to control are more acceptable than those they feel are beyond their control. When prevention

TABLE 11.2

EPA Cancer Working Group Consensus Ranking of Environmental Problem Areas on the Basis of Population Cancer Risk

Rank	Problem Area	Selected Comments
1 (tied)	Worker exposed to chemicals	About 250 cancer cases per year, estimated based on exposure to four chemicals; but workers face potential exposures to over 20,000 substances. Very high individual risk possible
2 (tied)	Indoor radon	Estimated 5,000–20,000 lung cancers annually from exposure in homes
3	Pesticide residues on foods	Estimated 6000 cancers annually, based on exposure to 200 potential oncogens
4 (tied)	Indoor air pollutants (non-radon)	Estimated 3500–6500 cancers annually, mostly due to tobacco smoke
5 (tied)	Consumer exposure to chemicals	Risk from four chemicals investigated is about 100–135 cancers annually from an estimated 10,000 chemicals in consumer products. Cleaning fluids, pesticides, particleboard, and asbestos-containing products are especially noted
6	Hazardous/toxic air pollutants	Estimated 2000 cancers annually based on an assessment of 20 substances
7	Depletion of stratospheric ozone	Ozone depletion projected to result in 10,000 additional annual deaths. Not ranked higher because of the uncertainties in future risk
8	Hazardous waste sites, inactive	Cancer incidence of 1000 annually from six chemicals assessed. Considerable uncertainty since their risk is based on extrapolation from 35 sites to about 25,000 sites
9	Drinking water	Estimated 400–1000 annual cancers, mostly from radon and trihalomethanes
10	Application of pesticides	Approximately 100 cancers annually; small population exposed but high individual risks
11	Radiation other than radon	Estimated 360 cancers per year. Mostly from building materials. Medical exposure and natural background levels are not included
12	Other pesticide risks	Consumer and professional exterminator uses estimated to produce 150 cancers annually. Limited data available for analysis
13	Hazardous waste sites, active	Probably fewer than 100 cancers annually. Estimates sensitive to assumptions regarding proximity of future wells to waste sites
14	Nonhazardous waste sites, industrial	No real analysis performed. Ranking based on consensus of professional opinion
15	New toxic chemicals	Difficult to assess; performed by consensus
16	Nonhazardous waste sites	Estimated 40 cancers annually, not including municipal surface impoundments
17	Contaminated sludge	Preliminary results estimate 40 cancers annually, mostly from incineration and landfilling

(continued)

TABLE 11.2 (continued)

EPA Cancer Working Group Consensus Ranking of Environmental Problem Areas on the Basis of Population Cancer Risk

Rank	Problem Area	Selected Comments
18	Mining waste	Estimated 10–20 cancers annually, largely due to arsenic. Remote locations and small population exposure reduce overall risk though individual risk may be high
19	Releases from USTs	Preliminary analysis based on benzene indicates low cancer incidence (<1/yr)
20	Nonpoint source discharges to surface water	No quantitative analysis available. Judgment employed
21	Other groundwater	Lack of information; individual risks considered less than 10^{-6} , with rough estimate of total population risk at <1/yr
22	Criteria air pollutants	Excluding carcinogenic particles and VOCs (included under hazardous/toxic air pollutants). Ranked low because remaining criteria pollutants have not been shown to be carcinogens
23	Direct point-source discharges to surface water	No quantitative assessment available. Only ingestion of contaminated seafood was considered
24	Indirect point-source discharges to surface water.	Same as the previous ranking
25	Accidental release, toxics	Short duration exposure yields low cancer risk. Noncancer health effects of much greater concern
26	Accidental releases, oil spills	See the previous ranking. Greater concerns for welfare and ecological effects

Source: U.S. EPA, *Unfinished Business: A Comparative Assessment of Environmental Problems, Overview Report*, EPA-230-2-87-025a, Office of Policy Analysis, Office of Policy, Planning and Evaluation, Washington, DC, 1987.

Not ranked: Biotechnology, global warming, other air pollutants, discharges to estuaries, coastal waters and oceans, discharge to wetlands.

is in the hands of the individual, the risk is perceived much lower than when prevention is in the hands of the government. For example, a person can choose what they eat, but they cannot control what is in the municipal drinking water.

3. *Fairness.* Risks that seem to be unfairly shared are believed to be more hazardous. People who endure greater risk than their neighbors and do not gain anything from this higher degree of risk are generally outraged by this. If one is not getting anything from being exposed to a higher risk, why should others benefit?
4. *Process.* The public critically assesses the process used by a regulatory agency and/or responsible party and asks questions such as: Are they trustworthy or dishonest, concerned or arrogant? If the

TABLE 11.3

Ranking Risks: Reality and Perception

League of Women Voters	Activity or Technology	Risk Experts
1	Nuclear power	20
2	Motor vehicles	1
3	Handguns	4
4	Smoking	2
5	Motorcycles	6
6	Alcoholic beverages	3
7	General (private) aviation	12
8	Police work	17
9	Pesticides	8
10	Surgery	5
11	Firefighting	18
12	Large construction	13
13	Hunting	23
14	Spray cans	26
15	Mountain climbing	29
16	Bicycles	15
17	Commercial aviation	16
18	Electric power (nonnuclear)	9
19	Swimming	10
20	Contraceptives	11
21	Skiing	30
22	X-rays	7
23	High school and college football	27
24	Railroads	19
25	Food preservatives	14
26	Food coloring	21
27	Power motors	28
28	Prescription antibiotics	24
29	Home appliances	22
30	Vaccinations	25

Source: Ayyub, B.M., *Risk Analysis in Engineering and Economics*, Chapman and Hall, Boca Raton, FL, p. 42, 2003. With permission.

governing agency tells the community what is going on before decisions are made, the public feels more at ease and less at risk. They also favor and feel safer when dealing with a company that listens and responds to community concerns.

5. *Morality*. Society has decided that pollution is not only harmful, it is evil. Talking about cost-risk tradeoffs sounds cold-hearted when the risk is morally relevant to the general public.

6. *Familiarity.* Risks from exotic technologies create more dread than do those involving familiar ones. "A train wreck that takes many lives has less impact on people's trust of trains than would a smaller, hypothetical accident involving recombinant DNA, which is only perceived to have catastrophic mishaps" [8].
7. *Memorability.* An incident that remains in the public's memory makes the risk easier to imagine and is, therefore, considered to be a higher risk than if they have little memory of it.
8. *Dread.* There are some illnesses that are feared more than others. Today, for example, there is greater fear associated with AIDS and cancer than there is with asthma.

These outrage factors are not distortions in the public's perception of risk. They are inborn parts of what is interpreted as risk. They are explanations of why the public fears pollutants in the air and water more than they do geological radon. The problem is that many risk experts resist the use of the public's "irrational fear" in their risk management.

A problem exists in the perception of risk because the experts' and laypeople's views differ. The experts usually base their assessment on mortality rates, while the laypeople's fears are based on the aforementioned "outrage" factors. In order to help solve this problem in the future, risk managers must work to make truly serious hazards more outrageous. One example is the ongoing concern for the risks involved with cigarette smoke. Another effort must be made to decrease the public's concern with low to modest hazards, i.e., risk managers must diminish "outrage" in these areas. In addition, people must be treated fairly and honestly so that trust is built between exposed communities and the risk managers and responsible parties.

Illustrative Example 11.13

The metabolism of ethyl alcohol may be considered to occur via a zero-order reaction (i.e., its elimination occurs linearly with time) [17]. If a person is able to metabolize approximately 10 mL of alcohol per hour, how long is required to eliminate the effects and associated risk of eight pints of beer containing 3.2% alcohol? Assume that the volume of a pint of beer is 530 mL.

Solution

The time for the elimination of the alcohol and the associated risks associated with intoxication can be estimated as follows:

$$\text{Time for elimination, } t = \frac{\text{Total dose}}{\text{Rate of elimination}} \quad (11.12)$$

$$t = (8 \text{ pints of beer}) \left(\frac{530 \text{ mL}}{\text{pint of beer}} \right) \frac{(3.2\% \text{ alcohol})}{(10 \text{ mL / h})}$$

$$t = \frac{135.6 \text{ mL ethanol}}{10 \text{ mL / h}} = 13.6 \text{ h}$$

Illustrative Example 11.14

An exponential, first-order decay reaction can be described using either a first-order reaction rate constant, k_1 , or a half-life ($t_{1/2}$). The equation that relates these two parameters is as follows:

$$t_{1/2} = \frac{0.693}{k_1} \quad (11.13)$$

Exponential decay of a chemical can be expressed by the following equation [17]:

$$N = N_0 e^{-k_1 t} \quad (11.14)$$

where

N_0 is the initial amount or concentration of the chemical

N is the amount or concentration of the chemical at time t

As part of a health risk assessment study, determine how much of a 100 g sample of polonium, Po-210, is left after 5.52 days using

1. The reaction rate coefficient
2. The half-life

Also consider the percent error between the two methods. The half-life of Po-210 is 1.38 days.

Solution

To answer the first part of this question, the reaction rate coefficient is first determined using Equation 11.13 as follows:

$$k_1 = \frac{0.693}{t_{1/2}} = \frac{0.693}{1.38 \text{ day}} = 0.502/\text{day}$$

From Equation 11.14, the amount of substance left after 5.52 days is calculated as follows:

$$N = N_0 e^{-k_1 t} = (100) e^{-(0.502)(5.52)} = 6.26 \text{ g}$$

To answer the second part of this question, the first step is to determine how many half-lives the sample has undergone in the given time period:

$$\text{Number of half-lives} = \frac{5.52 \text{ days}}{1.38 \text{ days half-life}} = 4.0 \text{ half-lives}$$

Therefore, in a 5.52 day period, the 100g sample has undergone four half-lives.

The amount of the substance left after four half-lives is calculated as follows:

$$(0.5)^4 (100 \text{ g}) = 6.25 \text{ g}$$

Since the two equations are, in principle, identical to each other, there should be no difference between the two values. The small difference between the two results arises because of round-off error. Either approach is valid in determining the decay of a substance over time via first-order reactions.

Illustrative Example 11.15

A local nuclear utility has hired you to conduct a health risk assessment that is concerned with a radioactive release from a reactor. The probability of the continuous release is 10^{-2} /year.

An earlier study indicated that:

1. 1,000 of the 10,000 exposed individuals located within 1 mile of the plant will die
2. 100 of the 100,000 exposed individuals located between 1 and 5 miles of the plant will die
3. 10 of the 1,000,000 exposed individuals located between 5 and 20 miles of the facility will die

Calculate the health risk associated with the emission. (Note that this is an extension of Illustrative Example 10.15.)

Solution

The result is provided in Table 11.4. Note that the local risk near the utility is unacceptably high, i.e., 10^{-3} , while the local risk at a distance significantly displaced from the reactor is low, i.e., 10^{-7} . The overall risk, OR, to the total population exposed is given by

$$OR = \frac{11.1}{1,110,000} = 10 \times 10^{-6} = 10^{-5}$$

TABLE 11.4
Illustrative Example 11.15 Risk Calculation

Location (Miles)	Number of Exposed Individuals	Number of Exposed Individuals That Will Die	Annual Risk of Deaths, Deaths × Probability of Release	Local Risk of Annual Deaths	Overall Annual Risk
<1	10,000	1000	(1000)(0.01) = 10	10/10,000	10/1,110,000
1–5	100,000	100	1.0	1.0/100,000	1.0/1,110,000
5–20	1,000,000	10	0.1	0.1/1,000,000	0.1/1,110,000
Total	1,110,000	1110	11.1		

This is excessive if the standard for protection of the general public from health risks is 1 in a million, particularly if the end point for predicted effects is death.

Illustrative Example 11.16

Refer to the previous illustrative example. Translate the results of this problem to a figure similar to that provided in Figures 4.1 and 7.1.

Solution

The health risk assessment flow chart for this problem is given as Figure 11.1.

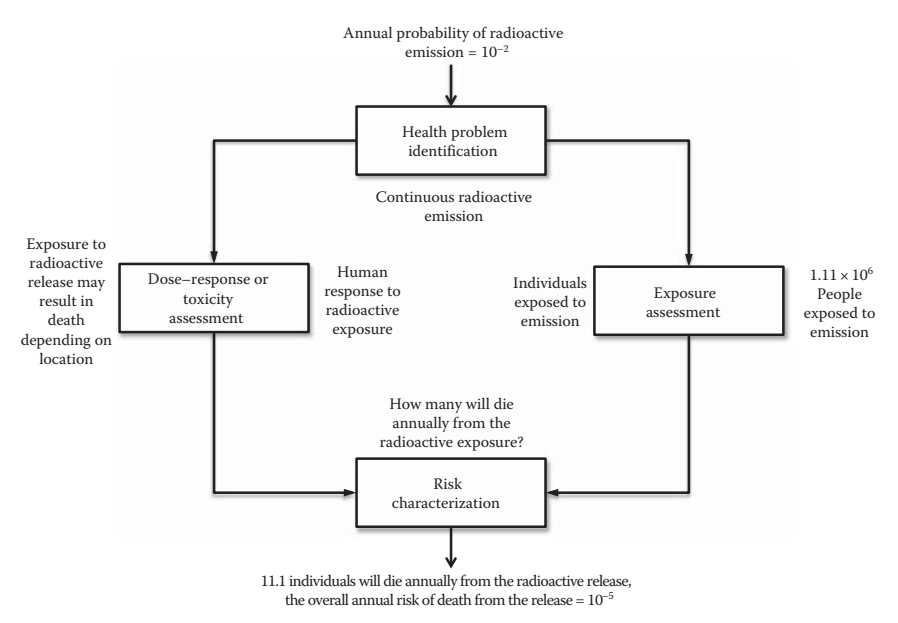


FIGURE 11.1
Health risk assessment flow chart for Illustrative Example 11.16.

Illustrative Example 11.17

Dupont and Theodore (DAT) Associates have been requested to conduct a health risk assessment at a chemical plant that is concerned with an EtO release as described in Illustrative Example 10.14. The annual probability of the continuous emission occurring is 10^{-5} ; the toxic level of EtO exposure is $0.33 \mu\text{g/L}$, and downwind concentrations from the release were calculated in Illustrative Example 10.14 using the Pasquill–Gifford model. The solution to Illustrative Example 10.14 indicates that of a total of 50 people are within the plant boundary when the release occurs, 10 individuals are within the critical zone where the toxic gas will travel after the release. Of these 10 potentially affected individuals, five are located 600m downwind of the emission source and will die, while the remaining five individuals are located 350m downwind and are not exposed to toxic levels of the chemical due to the release of the EtO from an elevated source and thus will not die.

DAT Associates have been specifically requested to calculate the average annual individual health risk based on the number of individuals potentially affected as well as the average risk based on all other individuals within the plant boundary.

The total annual risk, TAR, for the process, measured in terms of the average annual total number of people that will die, is obtained by multiplying the number of people in local critical zones that will die by the probability P of the event affecting that zone and summing the results. The average annual risk, AAR, based only on the “potentially affected” people downwind of the source, is obtained by dividing the TAR by the number of all people in the potentially critical zones. The average annual individual risk, AAIR, is determined based on all the individuals within the plant boundary.

Solution

For this release scenario, the TAR is calculated as:

$$TAR = \sum_{\text{Critical Zone } i} (\text{Number exposed that will die}) (\text{Probability of release})$$

$$\begin{aligned} TAR &= [(5 \text{ People in Zone 1}) + (0 \text{ People in Zone 2})] (1 \times 10^{-5}) \\ &= (5)(10^{-5}) = 5 \times 10^{-5} \end{aligned}$$

Since 10 people are located in the critical zones that are potentially affected by the release, the AAR is determined as follows:

$$AAR = \frac{TAR}{10} = \frac{5 \times 10^{-5}}{10} = 0.5 \times 10^{-5} = 5 \times 10^{-6}$$

Using the total number of people located at the plant site during the release, the average individual risk is now based on 50 rather than 10 individuals and is calculated as

$$AAIR = \frac{TAR}{50} = \frac{5 \times 10^{-5}}{50} = 0.1 \times 10^{-5} = 1 \times 10^{-6}$$

Once again, and as noted in Illustrative Example 10.14, the atmospheric dispersion calculation was based on one “average” meteorological condition, and these risk numbers could be modified based on the probability that this “average” condition occurs.

Illustrative Example 11.18

With reference to Illustrative Example 11.17, generate a figure similar to that provided in Figures 4.1 and 7.1 that contain the information and results of this previous example.

Solution

The solution is provided in Figure 11.2.

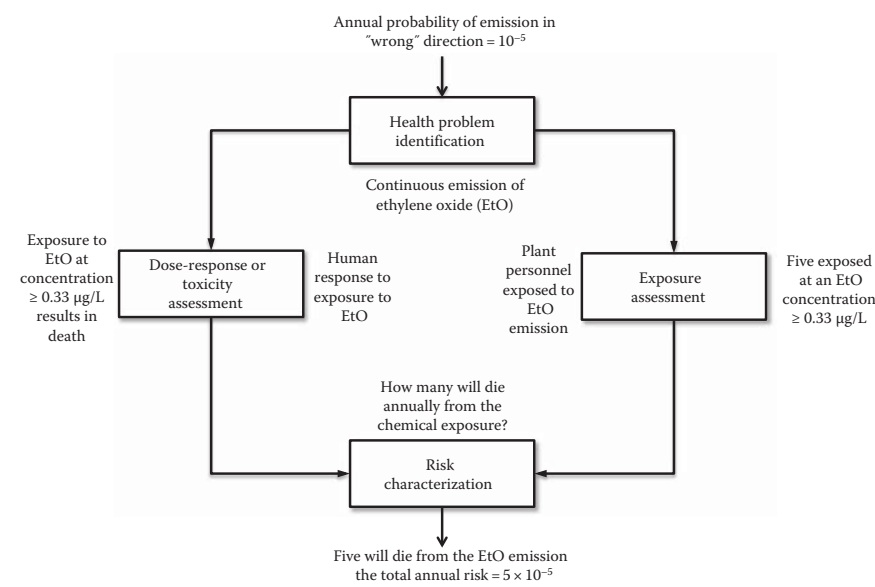


FIGURE 11.2
Chemical plant health risk assessment flow chart for Illustrative Example 11.18.

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Part III

Hazard Risk Assessment

Accidents will occur in the best-regulated families.

Charles Dickens (1812–1870)
David Copperfield, Chapter 28

Wherein I spake of most disastrous chances,
Of moving accidents by flood and field,
Of hair-breadth 'scapes i' the imminent deadly breach.

William Shakespeare (1564–1616)
Othello, Act I, Scene 3, Line 134

12

Introduction to Hazard Risk Assessment

12.1 Introduction

Risk assessment of accidents serves a dual purpose. It estimates the probability that an accident will occur and also assesses the severity of the consequences of an accident. Consequences may include damage to the surrounding environment, financial loss, injury, or loss of life. This chapter is primarily concerned with introducing the reader to the methods used to identify these hazards and the causes and consequences of accidents. Issues dealing with health risk assessments (HRA) have been explored in Part II. Risk assessment of accidents (or hazard risk assessment [HZRA]) provides an effective way to help ensure that a mishap either does not occur or reduces the likelihood of severe consequences as a result of an accident. The result of the risk assessment allows concerned parties to take precautions to prevent an accident before it happens.

There are other classes of environmental health risks that do not pertain to chemicals but are an integral part of HZRA. For example, health problems can arise immediately/soon after a hazard, such as a hurricane or earthquake, that can leave local inhabitants without potable water for an extended period. This class of environmental health risks can be determined by replacing the toxicity—exposure assessment steps in Figures 4.1 and 7.1 with the probability of occurrence—consequence(s) steps. The calculational approach then becomes similar to that provided earlier in Figure 4.2 for hazard risk problems. This point will be noted as the reader proceeds through this part of the book.

Regarding definitions, the first thing an individual needs to know is what exactly is an accident. An *accident* can be defined as an unexpected event that has undesirable consequences [1]. The causes of accidents have to be identified in order to help prevent accidents from occurring. Any situation or characteristic of a system, plant, or process that has the potential to cause damage to life, property, or the environment is considered a *hazard*. A hazard can also be defined as any characteristic that has the potential to cause an accident. The severity of a hazard plays a large part in the potential amount of damage a hazard can cause if it occurs. *Risk* is the probability that

human injury, damage to property, damage to the environment, or financial loss will occur. An *acceptable risk* is a risk whose probability is unlikely to occur during the lifetime of the plant or process. An acceptable risk can also be defined as an accident that has a probability of occurring with negligible consequences.

Risks can be ranked qualitatively in categories of high, medium, and low. Risk can also be ranked quantitatively as an annual number of fatalities per million affected individuals. This is normally denoted as a number times one millionth. For example, 3×10^{-6} indicates that on average three workers will die every year out of 1 million individuals. Another quantitative approach that has become popular in industry is the fatal accident rate (FAR) concept. This defines the number of fatalities over the lifetime of 1000 workers as a result of a given accident. The lifetime of a worker is defined as 10^5 h, which is based on a 40 h workweek over a working lifetime of 50 years. A FAR of 3.0 means that there are three deaths for every 1000 workers over a 50 year period. A reasonable FAR for a chemical plant is 3.0 with 4.0 usually taken as a maximum acceptable value. Interestingly, the FAR for an individual at home is approximately 3.0.

To summarize, the key questions that normally arise during the HZRA process are as follows:

1. What can go wrong?
2. What are the probabilities and causes associated with the accident?
3. What are the consequences?
4. What is the likelihood of the accident and/or risk?

The remaining chapter contents listed below will attempt to address these four questions in the analysis of industrial/plant applications.

Risk evaluation process for accidents

Hazard identification

Probability and causes of accidents

Consequences of accidents

Hazard risk characterization

Illustrative Example 12.1

Qualitatively define an accident.

Solution

As described earlier, an accident is an unexpected event or hazard that, when it occurs, has undesirable consequences to human health, the environment, and/or results in property damage and financial loss.

Illustrative Example 12.2

Discuss how hurricanes can lead to industrial accidents.

Solution

High winds, torrential rain, extreme high tides, lightning, and occasional tornadoes, which are all associated with hurricanes, can cause accidents to occur in chemical plants, refineries, utilities, offshore oil wells, etc. An HZRA can determine if adequate control, containment, safety, etc., can be maintained during such an event. This subject receives additional treatment in Part IV.

Illustrative Example 12.3

Describe the differences between catastrophic failure, degraded failures, and incipient failure.

Solution

The differences in failures can be defined as follows:

Catastrophic failure—a sudden failure where one or more fundamental functions have been terminated.

Degraded failure—a failure that occurs over time. Unlike catastrophic failure, a degraded failure does not terminate a function. It only impedes a function. This may result in undesired output and overtime if not fixed. It will eventually become a catastrophic failure if not corrected.

Incipient failure—a failure that can result in a catastrophic failure due to improper design of the equipment if left unattended.

12.2 Risk Evaluation Process for Accidents

There are several steps in evaluating the risk of an accident (see Figure 12.1).

A more detailed figure is presented in Figure 12.2. If the system in question is a chemical plant, specific steps to follow in the risk evaluation process are listed in the following:

1. A brief description of the equipment and chemicals used in the plant is needed.
2. Any hazard in the system has to be identified. Hazards that may occur in a chemical plant include:
 - a. Fire
 - b. Toxic vapor releases
 - c. Slippage
 - d. Corrosion

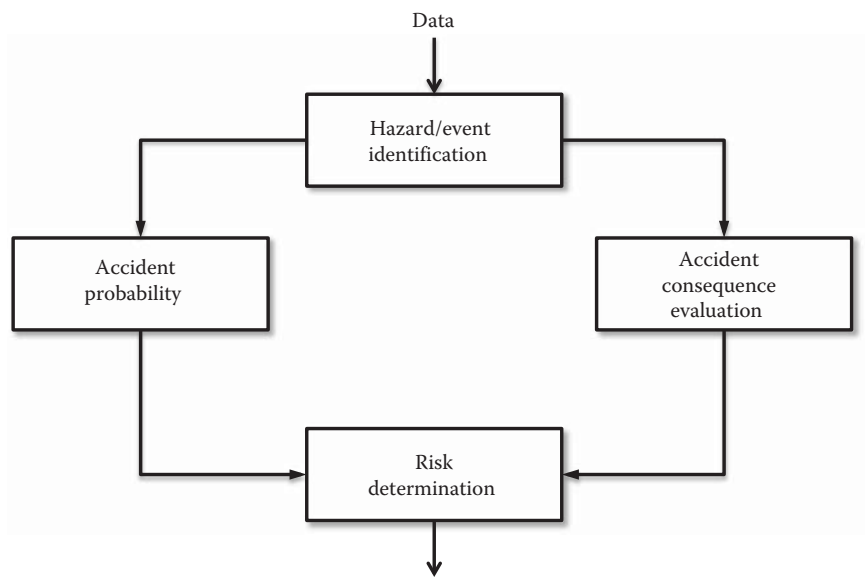


FIGURE 12.1
Simplified HZRA flowchart.

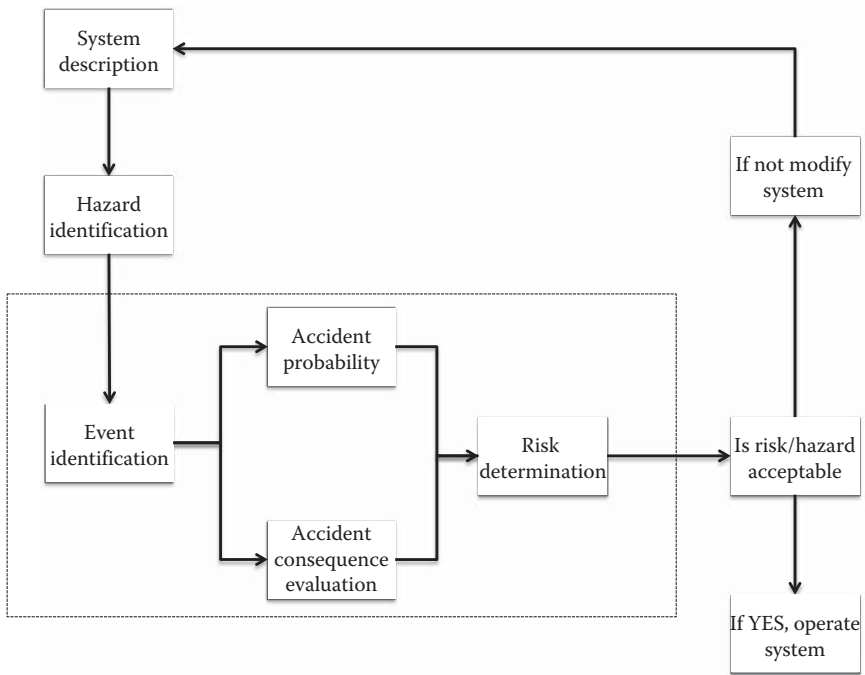


FIGURE 12.2
HZRA flowchart for a chemical plant.

- e. Explosions
 - f. Rupture of pressurized vessels
 - g. Runaway reactions
3. The event (or series of events) that will initiate an accident has (have) to be identified. An event could be a failure to follow correct safety procedures, improperly repaired equipment, or failure of a safety mechanism.
 4. The probability that the accident will occur has to be determined. For example, if a chemical plant has a 10 year life, what is the probability that the temperature in a reactor will exceed the specified temperature range over that lifetime? The probability can be ranked qualitatively from low to high. A low probability means that it is unlikely for the event to occur in the life of the plant. A medium probability suggests that there is a possibility that the event will occur. A high probability means that the event will likely occur during the life of the plant.
 5. The severity of the consequences of the accident must be determined. This will be described in detail later.
 6. If the probability of the accident and the severity of its consequences are low, then the risk is usually deemed acceptable and the plant should be allowed to operate. If the probability of occurrence is too high or the damage to the surroundings is too great, then the risk is usually unacceptable and the system needs to be modified to minimize these effects.

As indicated in Figure 12.2, the heart of the HZRA approach is enclosed in the dashed box comprising Steps 3 through 6. The algorithm allows for reevaluation of the process if the risk is deemed unacceptable (the process is repeated after system modification starting with Step 1).

Once again, it is important to note that an accident generally results from a sequence of events. Each individual event, therefore, represents an opportunity to reduce the frequency, consequence, and/or risk associated with the accident culminating from the individual events.

Illustrative Example 12.4

Discuss the various phases of an HZRA as it applies to a tornado.

Solution

The tornado is the hazard problem. The probability of encountering a tornado is the same whether one lives in a mobile home or in a below-ground shelter at the same location. However, the consequences are more severe for the mobile home. The risk associated with the tornado is therefore significantly higher for the mobile home since the belowground

shelter provides better safeguards against the hazard problem. From this analysis, one notes that the risk associated with the hazard problem can be reduced by applying different levels of safeguards.

Illustrative Example 12.5

Describe some of the uncertainties that can arise in preparing a description of a system.

Solution

Uncertainties can include:

1. Process descriptions or drawings that are incorrect or out of date
2. Procedures that do not represent actual operation
3. Weather data from the nearest available site that may be inappropriate for the system location under study
4. Site area maps and population data that may be incorrect or out of date

12.3 Hazard Identification

Hazard or event identification provides information on situations or chemicals and their releases that can potentially harm the environment, life, or property. Information that is required to identify these chemical hazards includes chemical identities; quantities and location of chemicals in question; and specific chemical properties such as boiling points, ignition temperatures, and toxicity to humans. There are several methods used to identify hazards. The methods that will be discussed here include the process checklist and the hazard and operability study (HAZOP).

A process checklist evaluates equipment, materials, and safety procedures [1]. A checklist is composed of a series of questions prepared by an engineer who knows the procedure or process being evaluated. It compares what is in the actual plant to a set of safety and company standards. Some questions that may be on a typical checklist are as follows:

1. What safety factor was used to design the equipment?
2. Does the spacing of the equipment allow for ease of maintenance?
3. Are there pressure relief valves on the equipment in question?
4. How toxic are the materials being used in the process and is there adequate ventilation to reduce potential vapor hazards?
5. Will any of the materials cause corrosion to the pipe(s)/reactor(s)/system?

6. What precautions are necessary for flammable materials?
7. Is there an alternate exit in case of fire?
8. If there is a power failure, what fail-safe procedure(s) does the process contain?
9. What hazard is created if any piece of equipment malfunctions?

These questions and others are answered and analyzed, and changes are made to reduce the risk of an accident based on the answers. Process checklists should be updated and audited at regular intervals.

A HAZOP study is a systematic approach to recognizing and identifying possible hazards that may cause failure of a piece of equipment or process [2]. This method utilizes a team with diverse professional backgrounds to detect and minimize hazards in a plant. If a process is being evaluated, it is divided into smaller processes (subprocesses). Guidewords are used to relay the degree of deviation from the subprocesses' intended operation or purpose. The guidewords can be found in Table 12.1. The causes and consequences of the deviation from the process are determined. If there are any recommendations for revision, they are recorded and a report prepared. The basic steps of a HAZOP study are as follows [2]:

1. Define objectives.
2. Define plant limits.
3. Appoint and (if necessary) train a team.
4. Obtain complete preparative work (i.e., flow diagrams, sequence of events).
5. Conduct examination meetings that select subprocesses, agree on intention of subprocesses, state and record intentions, use guide words to find deviations from the intended purpose, determine the causes and consequences of deviations, and recommend revisions.

TABLE 12.1

Guide Words Used to Relay the Degree of Deviation from Intended Subprocess Operation

Guide Word	Meaning
No	No part of intended function is accomplished
Less	Quantitative decrease in intended activity
More	Quantitative increase in intended activity
Part of	The intention is achieved to a certain percent
As well as	The intention is accomplished along with side effects
Reverse	The opposite of the intention is achieved
Other than	A different activity replaces the intended activity

6. Issue meeting reports.
7. Develop recommendations.
8. Follow up on revisions.

There are other methods of hazard identification. A “what if” analysis presents certain questions about a particular hazard and then tries to find the possible consequences of that hazard. The *human-error* analysis identifies potential human errors that will lead to an accident. They can be used in conjunction with the two previously described methods. Several of these hazard identification methods are discussed in more detail in Chapter 14.

Illustrative Example 12.6

Is an explosion at a gas station a health problem or a hazard problem?

Solution

In line with the definition employed in this chapter, the explosion is classified as a *hazard* problem. A risk assessment calculation for this problem would apply procedures discussed in this part of the book.

Illustrative Example 12.7

An attendant is exposed to fugitive emissions at a gas station. Is this a health problem or a hazard problem?

Solution

In this case, the problem is of a *health* nature. A risk assessment calculation here would employ the procedures outlined in Part II.

Illustrative Example 12.8

Describe how static electricity can lead to an accident.

Solution

Static electricity is generated—almost always unintentionally—in numerous industries and operations. Charging and discharging of static electricity can serve as a source of ignition in the production or handling of explosive gases, vapors, or dusts. Slight modifications of a supposed fail-safe procedure or process can suddenly result in static electricity discharges and possible ignition(s) and explosions.

Illustrative Example 12.9

Describe some of the events/accidents that could occur at an offshore oil exploration and production rig.

Solution

Possible accidents involving flammable materials at the rig site could include

1. A release of pressurized flammable material, such as might be caused by a piping failure or a vessel failure, with subsequent vapor dispersion, radiant heat, or blast overpressure effects (from a vapor cloud explosion)
2. A release of a pressurized flammable material and an on-site vapor cloud explosion with blast overpressure effects
3. A release of a pressurized flammable material burning at the release source with radiant heat effects
4. An internal explosion of flammable vapors and the potential for projectile impacts
5. A release of flammable material into the atmosphere in the immediate offshore area
6. A release of flammable material into the surrounding water area

Accidents associated with offshore activities also receive treatment in Part IV.

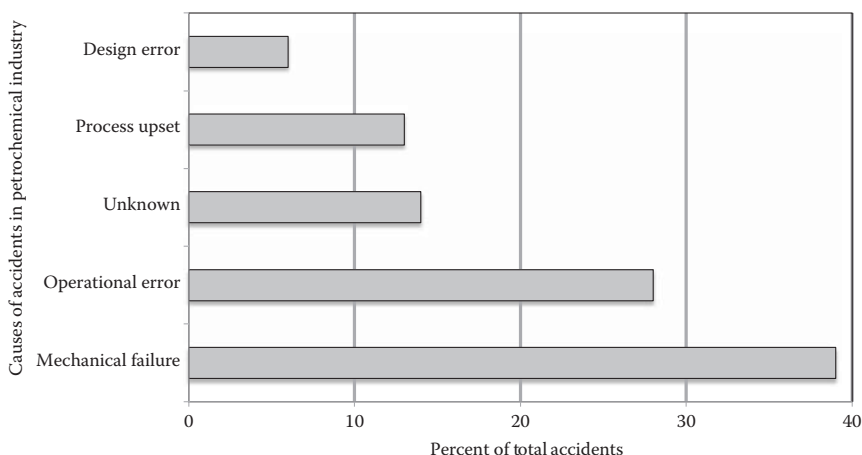
12.4 Probability and Causes of Accidents

The primary causes of accidents are mechanical failure, operational failure (human error), unknown or miscellaneous failures, process upsets, and design error. Figure 12.3 summarizes the *relative* number of accidents that have occurred in the petrochemical field (on a percentage basis) [3].

No matter what the root cause, there are three steps that normally lead to an accident:

1. Initiation
2. Propagation
3. Termination

The path that an accident takes through these three steps can be determined by means of a fault tree analysis [1]. A *fault tree* is a diagram that shows the path that a specific accident takes. The first item needed to construct a fault tree is the definition of the initial or initiating event. The initiating event is a hazard or action that will cause the process to deviate from normal operation. The next step is to define the conditions needed to result in propagation of this deviation, allowing the accident to occur. The propagation (e.g., the mechanical failure of equipment related to the accident) is discussed, and any other equipment or components that need

**FIGURE 12.3**

Causes of accidents in the petrochemical field.

to be studied are defined. This includes safety equipment that will bring about the termination of the accident. Finally, the normal state of the system in question is determined. The termination of an accident is the event that brings the system back to its normal operation. An example of an accident is a runaway reaction that might take place from an initiating event of the failure of a thermometer in the reactor. The temperature in the reactor could rise due to thermometer failure. Stopping the flow to the reactor and/or cooling the contents of the reactor are safety steps that could terminate the accident.

The companion to the fault tree is the *event tree*, a logic diagram that provides information on consequences, a topic treated briefly in the next section and in more detail in Chapter 15.

Illustrative Example 12.10

Consider the release of a toxic gas from a storage tank. List and discuss possible causes for the release.

Solution

Some possible causes for a toxic gas release from a storage tank are:

1. Rupture in the tank
2. Fire in the tank farm resulting in an explosion of the storage tank
3. Collapse of the tank due to an earthquake or other natural disaster
4. Rupture in the main line to the tank
5. A leak in a line or in the tank releasing its contents

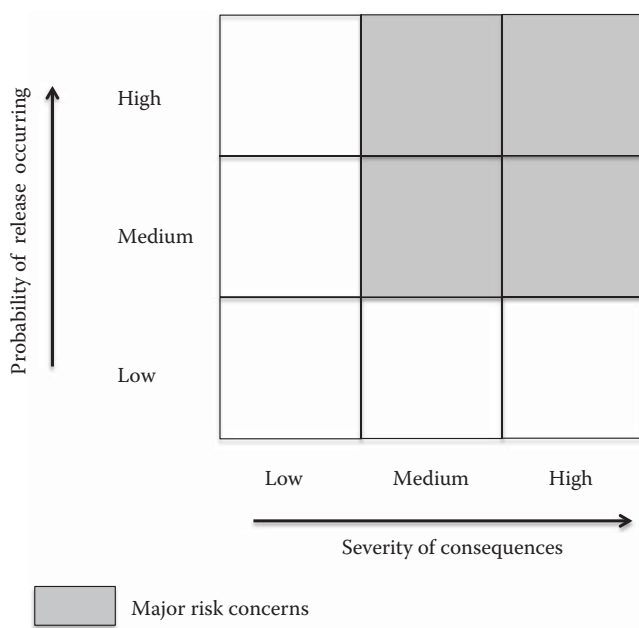
12.5 Consequences of Accidents

Consequences of accidents can be classified qualitatively by their degree of severity. A comprehensive quantitative assessment is beyond the scope of this chapter; however, information is presented in this chapter and available in the literature on this topic. Factors that help to determine the degree of severity of an accidental release are the concentration of the hazard that is released, the length of time that a person or the environment is exposed to the hazard, and the toxicity of the hazard. The worst-case consequence or scenario is defined as a conservatively high estimate of the most severe accident identified [1]. On this basis, one can rank the consequences of accidents into *low*, *medium*, and *high* degrees of severity [3]. A low degree of severity means that the hazard is nearly negligible, and the injury to persons, property, or the environment is observed only after an extended period of time. The degree of severity is considered to be medium when the accident is serious, but not catastrophic, the toxicity of the chemical released is moderate, or the concentration of a less toxic chemical is large enough to cause injury or death to persons and damage to the environment unless immediate action is taken. There is a high degree of severity when the accident is catastrophic or the concentrations and toxicity of a hazard are large enough to cause injury or death to many persons during a short exposure time, and there is long-term damage to the surrounding environment. Figure 12.4 provides a graphical, *qualitative* representation of the severity of consequences resulting from chemical accidents [3]. *Event trees*, to be discussed in Chapter 15, are often employed for this analysis.

12.6 Hazard Risk Characterization

There are various procedures available to the practicing engineer or scientist to characterize a hazard risk. These will be discussed in detail in Chapter 16. One such process is cause–consequence risk evaluation. It combines fault tree and event tree analyses to relate specific accident consequences to specific causes [1]. The process of cause–consequence evaluation usually proceeds as follows:

1. Select an event to be evaluated.
2. Describe the safety system(s)/procedure(s)/factor(s) that interfere with the propagation of events leading to the accident.
3. Perform an event tree analysis to identify the path or paths a series of events may follow leading up to an accident.

**FIGURE 12.4**

Qualitative probability-consequence analysis.

4. Perform a fault tree analysis to determine the safety function that failed.
5. Rank the results on the basis of the severity of the consequences.

As its name implies, cause-consequence analysis allows one to see how the possible causes of an accident and the possible consequences that result from that event interact with each other.

Once again, the subject of uncertainty surfaces although many of the methods of analyses are straightforward. Uncertainties can arise because of:

1. Inapplicable data
2. Data applicable only to the past
3. Data affected by maintenance policies, etc.

Illustrative Example 12.11

In attempting to solve problems, engineers usually apply what has come to be defined as the “engineering approach.” List some of the key considerations that are employed in this methodology.

Solution

Some aspects of the engineering approach related to HZRA include posing and answering the following questions:

Problem identification: What is the problem?

Problem location: Where is the problem?

Incident timing: When does the problem occur? When was it first observed?

Incident magnitude: How far does the problem extend? How many units are affected? How much of any one unit is affected?

Illustrative Example 12.12

In the case of an accident at a chemical plant, who will warn local residents about toxic emissions and provide for appropriate protection?

Solution

The Local Emergency Planning Committee (LEPC) (see Chapters 5 and 6) is tasked with developing warning systems, evacuation plans, and shelter-in-place instructions. Individual citizens can also ask the local plant to explain how their emergency response plans mesh with that of the LEPC. The plant must immediately report all incidents of chemical releases to the National Response Center (NRC), the State Emergency Response Commission (SERC), and the LEPC.

Illustrative Example 12.13

Qualitatively describe some of the “benefits” that arise following an accident/disaster.

Solution

Accidents/disasters can often become a spur to innovation. The trial and error process that is an integral part of advances in technology has, over time, resulted in the loss of much blood, significant pain and suffering, and the loss of millions of lives. It is not that engineers and scientists should seek out and embrace failures, but accidents/disasters, although appalling, are inevitable and a part of life. It is not surprising that technical individuals usually learn from these horrific acts to help prevent future mistakes. The bottom line is that the world as it is known today is the result of occurrences that many wish to forget. For example, the recent (2010) BP oil rig explosion will no doubt inspire technological advances in the offshore drilling arena. The same can be said for Bhopal, Flixborough, Chernobyl, the Titanic, the unspeakable results of 9/11, etc.

Illustrative Example 12.14

Provide some information on the ranking of risks.

Solution

The ranking of risk seems highly dependent upon the experience and familiarity of the risk ranker with the specific risk being considered. The public often worries about the largely publicized risks and thinks little about those that they face regularly. A classic risk characterization study presented in Part II, Chapter 11 compared the responses of two groups—15 national risk assessment experts and 40 members of the League of Women Voters—on the ranking of risks of 30 common activities and technologies ranging from smoking and alcoholic beverages to mountain climbing and private aviation [4]. This research produced striking discrepancies, as presented in Table 11.3. As noted, the League members rated nuclear power as the number 1 risk, while experts numbered it at 20; on the other extreme, the League ranked X-rays at 22, while the experts gave it a high relative risk rank of 7.

Illustrative Example 12.15

Describe some of the uncertainties associated with hazard identification.

Solution

Hazard identification uncertainties can include:

1. The incomplete recognition of major hazards
2. Important cases may be omitted when screening techniques are employed for the selection of hazards for further evaluation

The general subject of uncertainty was discussed in Parts I and II and will be addressed in greater detail later in this part of the book.

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3. J. Crowl and J. Louvar, *Chemical Safety Fundamentals with Applications*, Prentice-Hall, Upper Saddle River, NJ, 1990.
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13

Hazard/Event Problem Identification

13.1 Introduction

Hazard or event identification provides information on situations or chemicals and their releases, which can potentially harm the environment, life, or property. Information that is required to identify chemical hazards includes chemical identities; quantities and location of chemicals in question; and chemical properties such as boiling points, ignition temperatures, and toxicity to humans [1]. Obviously, the key word in this chapter is “identify,” and the first section in this chapter introduces the identification subject by reviewing the following topics:

- Process equipment
- Classification of accidents
- Fires, explosions, and hazardous spills

The last section of the chapter addresses hazard/event evaluation techniques and covers a number of methods used to identify some of the hazards common to chemical process and manufacturing industries.

Generally, the accidents in question will take the form of either a chemical release or a “disaster arising from a blast/fire fragment problem,” and some of the hazard/event evaluation techniques for these sorts of accidents include:

1. System checklists
2. Safety review/safety audit
3. “What if” analysis
4. Preliminary hazard analysis (PHA)
5. Hazard and operability (HAZOP) studies

An extensive treatment is provided on HAZOP studies since they are perhaps the most often used and successful technique for identifying hazards and hazardous events in the chemical process industry.

13.2 Process Equipment

This section provides details on a number of commonly used process units: reactors, heat exchangers, columns of various types (distillation, absorption, adsorption, evaporation, and extraction), dryers, and grinders. The purpose of each unit or operation and the many configurations in which the units can be found are also discussed.

Some important factors regarding a safe plant can be better understood if the reader is also familiar with other process equipment such as ancillary equipment, environmental equipment, utilities, and protective equipment. Process diagrams, which illustrate the various possible arrangements of plant equipment, valves, piping, and control systems, are also presented in this section. Plant siting and layout are discussed at the end of this section, detailing factors that can contribute to proper plant operation and increased safety. The reader is referred to Refs. [1,2] for more extensive details on the topics covered in this section.

13.2.1 Reactors

The *reactor* is often the heart of a chemical process. It is the place in the process where raw materials are usually converted into products, and reactor design is therefore a vital step in the overall design of the process. The treatment of reactors in this section is restricted to a discussion of the appropriate reactor types for a process. The design of an industrial chemical reactor must satisfy requirements in the following four fundamental areas [3]:

1. *Chemical factors.* These mainly involve the kinetics of the reaction. The design must provide sufficient residence time for the desired reaction to proceed to the required degree of completion.
2. *Mass transfer factors.* The reaction rate of heterogeneous reactions may be controlled by the rates of diffusion of the reacting species, rather than the chemical kinetics.
3. *Heat transfer factors.* These involve the removal or addition of the heat of reaction.
4. *Safety factors.* These involve the confinement of any hazardous reactants and products, as well as the control of the reaction and the process conditions.

13.2.2 Heat Exchangers

The transfer of heat to and from process fluids is an essential part of most chemical processes. The most commonly used type of heat transfer

equipment is the shell and tube heat exchanger. The chemical process industry uses four principal types of heat exchangers [3–5]:

1. *Double-pipe exchangers*: the simplest type, used for cooling and heating
2. *Shell and tube exchangers*: used for all applications
3. *Plate and frame exchangers (plate heat exchangers)*: used for heating and cooling
4. *Direct contact exchangers*: used for cooling and quenching

The word “exchanger” applies to all types of equipment in which heat is exchanged, but it is often used specifically to denote equipment in which heat is transferred between two process streams. An exchanger in which a process fluid is heated or cooled by a plant service stream is referred to as a *heater* or *cooler*.

13.2.3 Mass Transfer Equipment

13.2.3.1 Distillation Columns

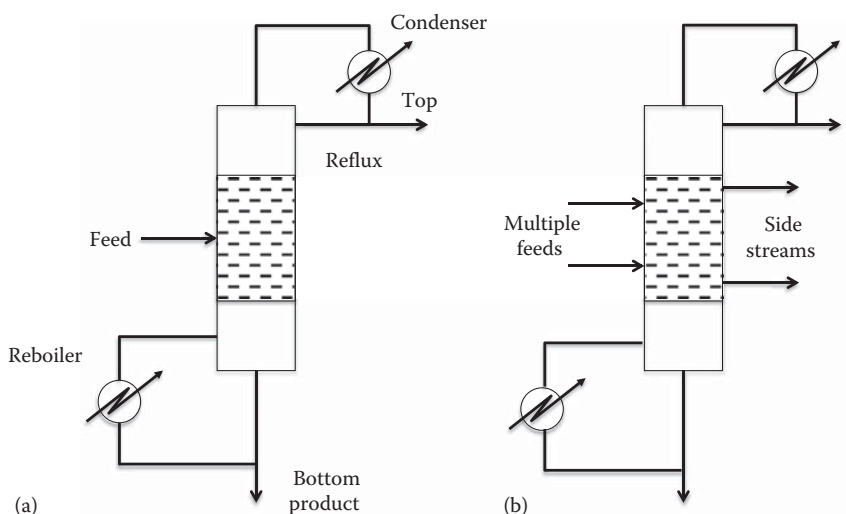
Distillation is probably the most widely used separation (mass transfer) process in the chemical and allied industries. Its applications range from the rectification of alcohol, which has been practiced since antiquity, to the fractionation of crude oil. The separation of liquid mixtures by distillation is based on differences in volatility between the components. The greater the relative volatility, the easier the separation of a liquid’s components [6].

Vapor flows up the column and liquid flows countercurrently down the column. The vapor and liquid are brought into contact on plates, or packing. Part of the condensate from the condenser is returned to the top of the column to provide liquid flow above the feed point (*reflux*). Part of the liquid from the base of the column is vaporized in the reboiler and returned to provide the vapor flow (see Figure 13.1).

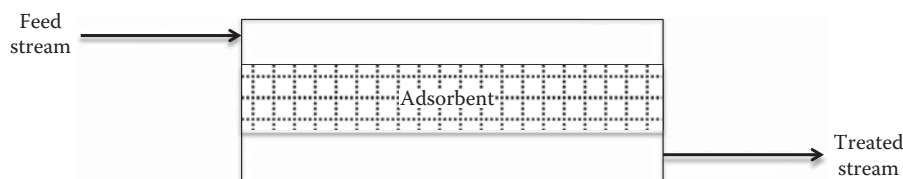
13.2.3.2 Adsorbers

Adsorption is influenced by the surface area of the adsorbent, the nature of the compound being adsorbed, the pH of the operating system, and the temperature of operation. These are important parameters to be aware of when designing or evaluating an adsorption process.

The adsorption process is normally performed in a column. The column is run as either a packed or fluidized bed operation. The adsorbent, after it has reached the end of its useful life, can either be discarded or regenerated. See Figure 13.2 for a typical process schematic of an adsorption column. For further information, the reader is directed to Refs. [1,2,6].

**FIGURE 13.1**

Distillation column. (a) Basic column; (b) multiple feeds and side streams.

**FIGURE 13.2**

Adsorber.

13.2.3.3 Absorbers

The process of *absorption* typically refers to the intimate contacting of a mixture of gases with a liquid so that part of one or more of the constituents of the gas will “dissolve” in the liquid. The contact usually takes place in some type of packed column.

Packed columns are used for the continuous contact between liquid and gas. The countercurrent packed column is the most common type of unit encountered in gaseous pollutant control for the removal of the undesirable gases, vapors, or odors. This type of column has found widespread application in the chemical industry. The gas stream moves upward through the packed bed against an absorbing or reacting liquid that is introduced at the top of the packing. This results in the highest possible efficiency since the concentration in the gas stream decreases as it rises through the column where there is constantly fresher liquid available for contact. This provides a

maximum average (or overall) driving force for the transfer process throughout the bed.

Other mass transfer operations include:

1. Evaporation
2. Extraction/leaching
3. Drying
4. Grinding
5. Ion exchange

The reader is referred to the literature for additional information on these and other mass transfer operations [6,7].

13.2.4 Ancillary Equipment

The discussion in this section focuses on devices for transporting gases and liquids to, from, or between units of process equipment. Some of these devices are simply conduits for the movement of material; *pipes, ducts, fittings, and stacks*; other devices control the flow of material; *valves*; and others provide the mechanical driving force for the flow; *fans, pumps, and compressors*. This section also covers storage facilities, holding tanks, material handling devices and techniques, and utilities (e.g., gas, steam, and water), along with air, water, and solid waste control equipment [7].

The most common conduits for fluids are pipes and tubing. Both generally have circular cross sections, but pipes tend to have larger diameters and thicker walls. Because of the heavier walls, pipes can be threaded, while tubing cannot. Process systems usually handle large flow rates that require the larger diameters associated with pipes.

While pipes and tubing are used as conduits for transporting liquids or gases, ducts are used only for gases. Pipes, with their thicker walls, can be used for flows at higher pressures; ducts are always thin walled and are generally used for gas flows close to ambient pressure. Although pipes are usually circular in cross section, ducts come in many shapes (circular, oval, rectangular, etc.). In general, ducts are larger in cross section than pipes because they carry fluids with low densities and high volumetric flow rates.

A fitting is a piece of equipment that has one or more of the following functions:

1. The joining of two pieces of a straight pipe (e.g., couplings and unions)
2. The changing of pipeline direction (e.g., elbows and tees)
3. The changing of pipeline diameter (e.g., reducers and bushings)
4. The joining of two streams (e.g., tees and y's)

Valves have two main functions in a pipeline: to control the amount of flow or to stop the flow completely. There are many different types of valves, but the most commonly used are the *gate valve* and the *globe valve*. The gate valve contains a disk that slides at right angles to the direction of flow. This type of valve is used primarily for on-off control of a liquid flow. Because small lateral adjustments of the disk cause extreme changes in the flow cross-sectional area, this type of valve is not suitable for adjusting flow rates. Globe valves, on the other hand, are designed for the control of flow, typically through the insertion of a beveled plug into a horizontal ring seal. Good control of flow is possible with a globe valve, but pressure loss through this valve is higher than with a gate valve.

The terms *fans* and *blowers* are often used interchangeably, and no distinction is made between them in the discussion that follows. Whatever is stated about fans equally applies to blowers. Strictly speaking, however, *fans* are used for low pressure (drop) operation, generally below 2 psi. *Blowers* are generally employed when pressure heads in the range of 2.0–14.7 psi are generated. Operation at even higher pressures requires *compressors*. Fans are usually classified as the *centrifugal* or the *axial-flow* type. In centrifugal fans, gas is introduced into the center of a revolving wheel (the eye) and is discharged at right angles to the rotating blades. In axial-flow fans, gas moves directly (forward) through the axis of rotation of the fan blades. Both types are commonly used in industry.

Pumps may be classified as *reciprocating*, *rotary*, or *centrifugal*. The first two are referred to as *positive-displacement* pumps because, unlike the centrifugal type, the liquid or semiliquid (slurry) flow is broken into small portions as it passes through the pump. Reciprocating pumps operate by the direct action of a piston on the liquid contained in a cylinder. The rotary pump combines rotation of the liquid with positive displacement. Centrifugal pumps are widely used in the process industry because of their simplicity of design, low initial cost, low maintenance, and flexibility of application. Centrifugal pumps have been built for high flow-low head conditions as well as to move as little as a few gallons per minute against a pressure of several hundred pound per square inch (psi).

Compressors operate in a similar fashion to pumps and have the same classifications: rotary, reciprocating, and centrifugal. An obvious difference between the two operations is the large decrease in volume resulting from the compression of a gaseous stream compared to the negligible change in volume caused by the pumping of a liquid stream. More details on transportation and storage of materials are available in Refs. [6,8].

13.2.5 Environmental Control Equipment

Air pollution equipment includes a range of units for the treatment of contaminated gases discussed earlier (adsorption, absorption, and distillation)

in addition to the following systems for the removal of particulate matter from contaminated gas streams [8,9]:

1. Electrostatic precipitators
2. Wet scrubbers
3. Baghouses (fabric filters)
4. Cyclones

Wastewater pollution equipment includes various reactor and equipment configurations carrying out a range of physical, chemical, and biological processes including [1,2]:

1. Oxidation/reduction/precipitation for the chemical removal of metals and other inorganic species from contaminated liquid streams
2. Activated sludge/anaerobic digestion/waste stabilization ponds for the biological removal of biodegradable organic material in liquid wastes
3. Centrifugation/filtration/coagulation and flocculation/sedimentation for the physical separation of particulate matter in liquid wastes

Equipment commonly used in industry for the thermal destruction of recalcitrant, hazardous, and toxic waste materials includes the following [1]:

1. Rotary kilns
2. Liquid injection incinerators
3. Fluidized bed incinerators
4. Multiple hearth furnaces

Pollution prevention approaches to environmental control and management are available in the literature [10].

13.2.6 Utilities

Today the word “utilities” generally designates the ancillary services needed in the operation of any production process. These services normally are supplied from a centralized facility and usually include the following:

1. Electricity
2. Steam for process heating
3. Cooling water
4. Water for general use

5. Demineralized water
6. Compressed air
7. Inert gas supplies
8. Refrigeration

Details regarding these utility services in industrial settings are available in Ref. [2].

13.2.7 Protective and Safety Systems

Protective systems are employed to reduce/eliminate hazards and risks and may be viewed as a special category of process equipment. The management of protective system's operation and maintenance and testing information should occur within the overall management systems for processes and equipment.

Provision for protection and safety equipment should be incorporated in the original plant design. The size of the plant, nature of the hazards, and potential exposures will determine the amount, kind, and location of this equipment.

Regarding fires, water is the primary extinguishing agent, and it should be available in adequate supply and at adequate pressure at all locations in the plant. The layout for various types of fire protection installations and the appropriate recommendations for their design are found in the standards of the National Fire Protection Association. Fire hydrants, hose lines, and automatic sprinkler and water spray systems should all be a part of the permanent equipment facilities of the plant.

Fire extinguishing systems can include foam, carbon dioxide, and dry chemicals. Wetting agents and high expansion foam have been used in some plant protection systems. All fire extinguishing systems should be evaluated for their potential health risks as well as their overall effectiveness before incorporation into a plant.

Since many chemical plants have severe potential health and hazard problems, it is essential to provide medical facilities and first aid stations in case rapid medical response is required. In addition, showers and eye wash stations are necessary in certain hazardous areas. Also, guards and covers should be provided for all moving equipment. Ten of the key protective equipment elements in a chemical process plant or manufacturing facility are listed below:

1. Pressure relief/vent collection
2. Release devices (flares, scrubbers, etc.)
3. Plant equipment isolation

4. Critical alarms/interlocks
5. Fire detection/protection
6. Hazardous/toxic gas detection
7. Flame arrestors
8. Emergency system services
9. Appropriate grounding and bonding
10. Personal protection equipment

13.2.8 Process Diagrams

To the practicing engineer, particularly the chemical engineer, the process flow sheet is the key instrument for defining, refining, and documenting a chemical process. The process flow diagram (PFD) is the authorized process blueprint and provides the framework for specifications used in equipment designation and design. It is the single, authoritative document employed to define, construct, and operate a chemical process.

Beyond equipment symbols and process stream flow lines, there are several essential elements contributing to a process flow sheet. These include equipment identification numbers and names, temperature and pressure designations, utility designations, volumetric or molar flow rates for each process stream, and a material balance table pertaining to process flow lines. The process flow sheet may show additional information such as energy requirements, major instrumentation, and physical properties of the process streams. When properly assembled and employed, this type of process schematic provides a coherent picture of the overall process. It can point out deficiencies in the process that may have been overlooked earlier in the study, for example, by-products (undesirable or otherwise) and recycle needs. Basically, the flow sheet symbolically and pictorially represents the interrelations among the various flow streams and equipment, and permits easy calculations of material and energy balances. A number of symbols are universally employed to represent equipment, equipment parts, valves, piping, etc. These symbols obviously reduce, and in some instances replace, detailed written descriptions of the process. Note that many of the symbols are pictorial, which improves the descriptive power of the document.

A flow sheet usually changes over time with respect to the degree of sophistication and the details it contains during the design process. A crude flow sheet may initially consist of a simple, freehand block diagram offering information about the equipment only. A later version may include line drawings with pertinent process data such as overall and componential flow rates, utility and energy requirements, and instrumentation. During the final stages of a design project, the flow sheet will consist of a highly detailed *piping and instrumentation diagram (P&ID)*, which is covered in a later section.

For information on aspects of the design procedure, which is beyond the scope of this chapter, the reader is referred to Refs. [1–7].

In a sense, process flow sheets are the international language of the engineer, particularly the chemical engineer. Chemical engineers conceptually view a (chemical) plant as consisting of a series of interrelated building blocks that are defined as units or unit operations. The plant essentially ties together the various pieces of equipment that make up the process. Flow schematics follow the successive steps of a process by indicating where the pieces of equipment are located and when the material streams enter and leave each unit.

The *PFD* is a pictorial description of the process. It gives the basic processing scheme, the basic control concept, and the process information from which equipment can be specified and designed. It provides the basis for the development of the *P&ID* and also serves as a guide for the plant operator. The *PFD* usually includes:

1. Material balance data (may be on separate sheets)
2. Flow scheme equipment and interconnecting streams
3. Basic control instrumentation
4. Temperature and pressure at various points
5. Any other important parameters unique to each process

Data on spare and parallel equipment are often omitted. Valving is also generally omitted. A valve is shown only where its specification can aid in understanding intermittent or alternate flows. Instrumentation is indicated to show the location of variables being controlled and the location of the actuating device, usually a control valve.

The process *piping and instrumentation diagram*, or *P&ID*, which provides the basis for detailed design, offers a precise description of piping, instrumentation, and equipment. This key drawing defines the plant system; describes equipment; and shows all instrumentation, piping, and valving. It is used to train personnel and aids in troubleshooting during start-up and operation. The *P&ID* assigns item numbers to all equipment (e.g., towers, reactors, and tanks); gives dimensions of equipment and vessel elevations; and shows all piping, including line numbers, sizes, and specifications, and all valves. All instrumentation is covered, with relevant numbers, function, and types (i.e., an indication of electronic or pneumatic control, etc.).

13.2.9 Plant Siting and Layout

The proper location of a plant is as important to its success as the selection of a process. Important factors to be considered in the study of areas and sites

for plant location include raw materials, transportation, process water, waste disposal, and fuel and power availability, as well as prevailing weather conditions in the areas being considered [11].

Not only must many of these tangible factors, such as labor supply and raw material sources, be carefully considered but also a number of intangible factors must be evaluated. The selection of a plant site must be based on a very detailed study in which all factors are weighed as carefully as possible. Such a study often requires a substantial outlay of capital.

For many processes, one or more predominant factors effectively minimize the number of possibilities for plant location. Raw material and transportation costs may be such that a plant must be located near a raw material source. Thus, only the sites near to sources of raw material need be studied and these may be few in number. Similarly, labor requirements may be significant or unique enough to eliminate cities below a certain size. These and other factors serve as effective screening criteria that save both time and money when plant siting is being evaluated.

Many of the safety considerations associated with plant and process equipment and plant siting and layout can be better understood by performing an HAZOP study. HAZOP is covered in detail later in this chapter.

Illustrative Example 13.1

Discuss the various classes of heat exchangers [3,4].

Solution

The chemical process industry uses four principal types of heat exchangers:

1. *Double-pipe exchangers*: the simplest type with a concentric pipe arrangement used for cooling and heating; several units can be connected in series to extend their capacity.
2. *Shell and tube exchangers*: most commonly used for all applications in the chemical and allied industries; there are several advantages to this type of heat exchanger: large surface area in a small volume, good mechanical layout, reliance on well-established fabrication techniques, wide range of construction materials available, easily cleaned equipment, and well-established design procedures.
3. *Plate and frame exchangers (plate heat exchangers)*: used for heating and cooling in reactor off-gas quenching, vacuum condensers, desuperheating, and humidification.
4. *Direct contact exchangers*: used for cooling and quenching whenever the process stream and the coolant are compatible; the equipment used is basically simple and inexpensive.

The reader is referred to the literature for the description of other types of heat exchanger units [3,4].

Illustrative Example 13.2

What are potential consequences if a pinhole leak develops in a tube in the reboiler of a distillation column?

Solution

Potential consequences of a pinhole leak in this piece of process equipment are as follows:

1. Changes in pressure
2. Changes in temperature
3. Chemical reaction, with accompanying overpressure, overtemperature, and formation of other phases
4. Leakage of toxics/flammables to an undesirable location
5. Corrosion, embrittlement, or similar effect

Illustrative Example 13.3

List safety concerns (in the form of questions) associated with plant site location and layout.

Solution

1. Is there any exposure to or from other nearby plants from fire, noise, air pollution, stream pollution, or explosion hazards?
2. Is there adequate access for emergency vehicles?
3. Are major highways, airports, or congested areas near the plant site capable of blocking access roads at any time of the day?
4. Are access roads well engineered to avoid sharp curves? Are traffic signs provided?
5. Do adequate fences and gates enclose the plant?
6. Will toxic fumes or fires, explosions, or other accidents at the plant affect the surrounding community?
7. Is the plant well situated with regard to topography and adequate drainage?
8. Are utilities (water, gas, electricity, etc.) adequate?
9. Are waste disposal systems downwind from plant personnel and the surrounding community?
10. Are loading areas on the periphery of the plant away from any sources of ignition?
11. Will the local climate/weather (earthquake, flood, fog, hurricane, lightning, smog, snow, tornado, and very low temperatures) materially affect plant operations?
12. Is there a safe distance from the plant boundary to the fence?

Illustrative Example 13.4

Discuss the main differences between a PFD and a process P&ID.

Solution

The PFD is a pictorial description of the process. It gives the basic processing scheme, control concept, and process information from which equipment can be specified and designed. It provides the basis for the development of the process P&ID and also serves as a guide for the plant operator. The PFD usually includes the material balance data, flow scheme equipment and interconnecting streams, basic control instrumentation, temperature and pressure at various points, and any other important parameters unique to each process. The process P&ID provides the basis for detailed design. It offers a precise description of piping, instrumentation, and equipment. This key drawing defines the plant system, describes equipment, and shows all instrumentation, piping, and valving. It is used to train personnel and aids in troubleshooting during start-up and operation. The process P&ID assigns item numbers to all equipment (e.g., towers, reactors, and tanks); gives dimensions of equipment and vessel elevations; shows all piping, including line numbers, sizes, and specifications, and all valves. All instrumentation is described in detail with numbers, function, and type (i.e., whether electronic or pneumatically controlled).

13.3 Classification of Accidents

Classes of accidents that can result in financial and personal losses include more than just natural disasters such as earthquakes and tornadoes or occupational mishaps such as tripping and slipping. These, and several others, are reviewed in this section, including:

1. Equipment failures
2. Human error and occupational mishaps
3. Transport accidents
4. Electrical and computer failures
5. Nuclear accidents
6. Natural disasters

Although the terms “emergency” and “accident” have already been defined from a risk assessment point, they are now defined in relatively general terms to help the reader differentiate between the two and to understand their application to the general subject of process “occurrences.”

An *accident* is defined as an unexpected event or, alternately, an event that is not likely to occur. Accidents are usually uncontrolled events. They are the results of unforeseen circumstances and changes in otherwise controlled conditions.

An *emergency* is defined as a crisis or a sudden occasion that requires immediate remedial action to restore the previous (i.e., controlled) conditions. Therefore, an emergency precedes an accident and also encompasses it. Before an accident, there is an emergency or a pressing need to revert to or restore the previous conditions that would alleviate the potential for an accident. During an accident, there is an even more urgent need to alter existing conditions in a manner that will not only alleviate the hazardous or critical condition(s) that are causing the accident but that also will minimize the effects of the occurring accident.

Accidents, such as fires, explosions, toxic emissions, and hazardous spills, are dealt with separately in the next section. The decision to include these in a separate section was not as easy as one would expect since the topics of both these sections could be classified as accidents. However, in order to treat the accidents in a cause-and-effect manner, it was felt that fires, explosions, etc., could be considered an effect arising from the generic accidents discussed in this section.

13.3.1 Equipment Failures

The academic training of engineers with respect to plant equipment has traditionally focused on design and predicting performance. Little to no effort has historically been expended in attempting to answer the question:

WHAT CAN GO WRONG?

This question requires answers in today's high-tech environment. Failure to properly and realistically address and answer this question can result/lead to an

ACCIDENT!

Once an industrial accident has occurred, the responsible individual (usually the operator or engineer) should react as quickly as possible in a responsible manner (exercise good judgment) to detect and correct the situation and hopefully reduce and/or eliminate potential danger(s).

Industry now knows that equipment sometimes partially fails and sometimes catastrophically fails. In any event, it behooves the engineer to carefully and thoroughly examine the various pieces of plant equipment that can fail. A partial list of some of the more common equipment that can be expected to fail in a plant with some regularity is provided in the following. Details are available in Ref. [12].

1. Foundations
2. Structural steel
3. Vessels and tanks
4. Pumps

5. Compressors
6. Fans
7. Heat exchangers
8. Turbines
9. Electrical systems
10. Instrumentation and controls
11. Piping systems
12. Valves and joints
13. Mass transfer unit operations
14. Heaters and furnaces
15. Chemical reactors
16. Fire protection equipment
17. Safety equipment

Deviations, i.e., abnormal conditions that can lead to a failure and/or an accident, generally occur because of:

1. Abnormal temperatures
2. Abnormal pressures
3. Material flow stoppage
4. Equipment leaks
5. Equipment spills
6. Materials failure due to wear
7. Materials failure due to imperfections
8. Materials failure due to poor maintenance
9. Materials failure due to corrosion

Some specific operational failures include:

1. Blocked outlets
2. Opening/closing valves
3. Cooling water failure
4. Power failure
5. Instrument air failure
6. Thermal expansion
7. Vacuum problems

Specific comments/recommendations/procedures for the prediction, prevention, and/or management of potential failures of equipment that can be

found in a process plant are beyond the scope of this chapter, but details are available elsewhere [12,13].

Another area of concern is scale-up, where the term is generally assumed to represent the increase in size of a small plant, pilot plant, or experimental unit to a large or full-scale plant. Hazards (or problems of a general nature) may be absent from the smaller system but present in the larger system. One simple example is the effect of size changes on the surface area and volumes of reactors. If a system can be physically represented by a sphere, doubling its radius (or diameter) increases the volume-to-area ratio by a factor of 2.0. In this case, heat transfer requirements or concerns could change and produce a problem during scale-up.

13.3.2 Human Errors and Occupational Mishaps

Occupational mishaps are usually a function of three aspects of the work place: the human element, task variables (i.e., the job itself), and the environmental element. These three aspects are briefly addressed below.

13.3.2.1 Human Element

When evaluating human elements in relation to occupational mishaps, five factors must be taken into consideration [14–17].

1. *Sex.* Within a given job setting, a worker's sex may increase the individual's propensity for accidents and injuries. For example, if a job originally designed for male workers is opened to female workers, the possibility of increased proneness to injuries of certain types (e.g., back injuries) should be considered [14].
2. *Age.* Data seem to indicate that younger workers have a higher potential to become involved in accidents. This may be due to several factors, such as inexperience, often resulting in bad judgment, a tendency toward aggressiveness, and a willingness to take high risks. In addition, at the other end of the spectrum, older workers may begin to lose their eyesight, hearing, dexterity, and strength, which may also lead to higher accident and injury potential [14].
3. *Personality.* Personality factors such as tendency toward anger, discontent, excitability, and hostility, as well as a low order of adjustment and high impulsiveness can also contribute to maladjustments and accidents [14].
4. *Physical–physiological status.* A worker's physical and physiological capacity for work may have an impact on his or her accident and injury potential. For example, many accidents occur during the handling, lifting, and carrying of goods; frequently, the result is permanent injury (such as back trouble or hernia) and long periods of absence from work [14].

5. *Accident proneness.* The old notion that certain people are accident prone has been difficult to establish as fact. A more acceptable concept may be “accident liability,” which can be related to factors that often are temporary and do not depend primarily on personality traits such as work situation or stress [14].

Human error analysis is a procedure that evaluates the factors influencing the performance of operators, maintenance personnel, technicians, etc. Its purpose is to identify human errors and their accompanying effects. It has also been used to identify the cause of human errors. Kletz has an exceptional treatment of this topic in several of his chapters [14].

13.3.2.2 Task Variables

Hazards inherent in the job itself contribute to the overall accident potential of occupational mishaps. Within the category of task variables, there arise hazards that can be described as mechanical, electrical, and thermal.

1. *Mechanical hazards.* Injuries can arise from the improper use of hand tools, the use of defective tools, or the use of the wrong tools. Moving machinery also can cause accidents. Many accidents occur because isolation of the moving parts of mechanical equipment is incomplete, exposing workers to the possibility of catching a hand or piece of clothing in rotating machine parts.
2. *Electrical hazards.* If grounding and bonding systems are absent or inadequately maintained, or if electrical tool and equipment maintenance is inadequate, serious accidents can result. For example, cables and plugs are vulnerable to failure and require periodic inspection and maintenance. Wear occurs particularly at the point where a cable enters an electrical tool or plug.
3. *Thermal hazards.* These hazards include hot surfaces (and occasionally cold ones as well); fire produced by reacting substances; and flame contacts from heat-producing equipment, welding operations, etc.

13.3.2.3 Environmental Element

Injuries and occupational illnesses can be functions of the following environmental factors:

1. *Atmospheric hazards.* Examples are the presence of toxic airborne chemical substances and particulate matter, biological agents, noise, vibration, radiation, extremes of temperature and humidity, and lack of illumination.

2. *Workplace characteristics.* Examples include flammable and other hazardous materials, unsafe walking and working surfaces, plus workplace layout and design that can cause excessive strain on the worker. These environmental variables have a direct influence on the level of danger associated with a particular task. These variables may add to the danger inherent in an already dangerous task [14].
3. *Social factors.* The personalities of coworkers and supervisors are also factors to be considered when evaluating the workplace. The higher the employee morale, the lower the potential for accidents. Another factor is the relationship of one job to another, and whether a job requires the coordination of information, material, and human effort from other workers throughout the workplace.

In addition to natural disasters and occupational mishaps, the process industry is subject to “accidents” such as theft, vandalism, and terrorism. Very few events of these types occur. However, steps and precautions should always be taken to minimize their potential for occurrence and to cope with any damage that they might cause.

13.3.3 Transport Accidents

This section focuses on industrial accidents that are not plant related but that occur during the transport and storage of hazardous substances. Frequently, such accidents result in fires, explosions, and toxic releases that are discussed later in the chapter.

Fire is more likely than an explosion where there is a loss of containment of a flammable material from a railroad car, barge, ship tank, or from a pipeline. However, both unconfined vapor cloud explosions (UVCEs) and boiling liquid-expanding vapor explosions (BLEVEs) can occur as a result of transport accidents.

In addition to fires and explosions, the loss of containment of conventional toxic substances from a tank or pipeline may give rise to a large toxic gas cloud or may pollute water supplies. There is little published information on the extent to which ultratoxic substances are transported. In view of the danger of the contamination that may arise from even a small spill of such material, transport of a highly toxic substance is usually carried out by special arrangement. The initiating cause of transport accidents may lie with the cargo, the operations, or the transporter.

Cargo may catch fire, explode, or corrode the tank in which it is being transported and stored. The use of the same container to carry different chemicals is quite normal; it is fairly common practice with road tankers, barges, ships, and pipelines. This not only creates potential problems of incompatibility between substances carried but also means that carriers are less familiar with the substances being transported when their loads vary.

Thus, it is essential that all personnel involved in the transport of chemicals be thoroughly trained in the properties of the range of chemicals they might transport, their possible hazards, and the emergency procedures associated with each hazard if they do occur [16].

Accidents can occur when operations such as charging and discharging are incorrectly executed, when tanks are accidentally overfilled, or when cleaning procedures are not fully or completely executed, resulting in undesirable reactions from the mixing of incompatible chemicals.

Assessments of the comparative safety of the different modes of transport should take into account both the risk to the public and the risk to the terminal operators and transport crew. The transporter may be involved in a crash or derailment; drivers may be injured or killed. Thus, the events that can give rise to hazards include container failure, loading and unloading operations, and accidents.

Hazardous materials are generally moved via:

1. Roadways
2. Railways
3. Inland waterways (barges)
4. Pipelines
5. Seagoing tankers
6. Aircraft

Accidents of various types and various magnitudes can and have occurred in all of these transport methods. Details of necessary safety precautions and planning requirements specific to each of these transport modes are available in Ref. [13].

13.3.4 Electrical Failures

All wiring and electrical equipment in chemical plants should be installed in accordance with the National Electrical Code. Electrical equipment for use in hazardous locations should be certified by Underwriters Laboratories (or other testing organizations recognized by the authority having jurisdiction) for the conditions to be encountered.

The proper installation of electrical equipment is very important from the standpoint of safety. Electrical equipment should be grounded for protection of both personnel and equipment. Precautions should be taken to prevent flammable gases or vapors from traveling through conduits to a point of ignition. Adequate clearance or insulation should be provided between conduits and hot surfaces to prevent damage to wiring insulation. Lighting should be adequate for the purposes of good operational practices and conformance with standards [16].

Static electricity presents a dangerous source of ignition in hazardous chemical processing. Equipment must be properly bonded and grounded to minimize this danger. Lightning, a natural occurrence, is a hazard to electric power lines, structures, and hazardous chemical storage and process units. Sharp, high points on equipment should be avoided. Equipment should be shielded from lightning by protective grounding wires, rods, or masts.

From a basic physics standpoint, a circuit is a complete loop. Electric current can flow only if it returns to its source, i.e., completes the circuit. The path through which the current returns to its source is called the “return” or ground. The reason for the term “ground” is that the earth is literally used to provide the return path no matter what distance separates the equipment from the power source. Ground connections can be made to a cold water system as its components provide a reliable, low-resistance path for contact with the earth.

Shock occurs when the body becomes a part of the circuit, i.e., the current enters the body at one point and leaves at another [17]. Shock normally occurs in one of three ways. The person must come in contact with both wires of the electrical circuit, with one wire of an energized circuit and the ground, or with a metallic part that has become “hot” by being in contact with an energized wire while the person is also in contact with the ground.

Electrical accidents appear to be caused by any one or any combination of three possible factors: unsafe equipment, unsafe installation, or both; workplaces made unsafe by the environment; and unsafe work practices. Possible ways to protect people from the hazards caused by electricity include insulation, guarding, grounding, mechanical devices, and safe work practices.

Finally, when using electrically powered or controlled machines, the equipment as well as the electrical system itself must be properly grounded. Replacing frayed, exposed, or old wiring will also help protect the operator and others from electrical shocks or electrocution. Just as all power sources for machinery are potential sources of danger (and must be checked before use), high pressure systems also need careful inspection and maintenance to prevent possible failure from pulsation, vibration, or leaks. Such a failure could cause shocks, explosions, or flying objects.

13.3.5 Nuclear Accidents

Nuclear or radioactive materials are used in many applications throughout today's society. Radioactive materials are used to generate power in nuclear power plants and are used to treat patients in hospitals. The generators of radioactive waste in today's society are primarily the federal government, electrical utilities, private industry, hospitals, and universities. Although each of these generators uses radioactive materials, the waste that is generated by each of them may be very different and must be handled accordingly. Any material that contains radioactive isotopes in measurable quantities is considered nuclear or radioactive waste. For the purposes of

this discussion, the terms nuclear waste and radioactive waste will be considered synonymous.

Waste management is a field that involves the reduction, stabilization, and ultimate disposal of waste. Waste reduction is the practice of minimizing the amount of material that requires disposal. Some of the common ways in which waste reduction is accomplished are incineration, compaction, and dewatering [10]. The object of waste disposal is to isolate material from the biosphere, and in the case of radioactive waste, allow it some time to decay to sufficiently safe levels.

Although much still remains to be learned about the interaction between ionizing radiation and living matter, more is known about the mechanism of radiation damage on the molecular, cellular, and organ system level than most other environmental hazards. A vast amount of quantitative dose-response data have been accumulated throughout years of studying the different applications of radionuclides [10].

Several different mechanisms, most importantly alpha particle, beta particle, and gamma ray emissions, accomplish radioactive transformations. Each of these mechanisms is a spontaneous nuclear transformation. The result of these transformations is the formation of different stable elements. The kind of transformation that will take place for any given radioactive element is a function of the type of nuclear instability as well as the mass-energy relationship. The nuclear instability is dependent on the ratio of neutrons to protons; a different type of decay will occur to allow for a more stable daughter product. The mass-energy relationship states that for any radioactive transformation, the laws of conservation of mass and conservation of energy must be followed.

The response of humans to varying doses of radiation is a field that has been widely studied. The observed radiation effects can be categorized as *stochastic* or *nonstochastic* effects, depending upon the dose received and the time period over which such dose was received. Contrary to most biological effects, effects from radiation usually fall under the category of stochastic effects. The nonstochastic effects can be noted as having three qualities: a minimum dose or threshold dose must be received before the particular effect is observed; the magnitude of the effect increases as the size of the dose increases; and a clear, casual relationship can be determined between the dose and the subsequent effects.

Stochastic effects, on the other hand, occur by chance. Stochastic effects will be present in a fraction of the exposed population as well as in a fraction of the unexposed population. Therefore, stochastic effects are not unequivocally related to a noxious agent. Stochastic effects have no threshold. Any exposure will increase the risk of an effect but will not wholly determine if any effect will occur. Cancer and genetic effects are the two most common effects linked with exposure to radiation. Cancer can be caused by damage of a somatic (nonreproducing) cell, while genetic effects are caused when damage occurs to a germ cell that results in pregnancy.

13.3.6 Natural Disasters

An event may be labeled an accident through the assessment of the following factors:

1. Degree of expectedness
2. Degree of misjudgment
3. Degree of intention
4. Degree of warning
5. Degree of negligence
6. Degree of avoidability

Items 3 through 6 do not apply to natural accidents. Natural accidents are often termed “acts of God” and can include:

1. Floods
2. Lightning
3. Windstorms
4. Landslides
5. Earthquakes
6. Tornadoes
7. Hurricanes
8. Volcanic eruptions
9. Avalanches

Although accidents of these types occur infrequently, they may present a greater potential for loss than fires, explosions, or spills. Since natural disasters are difficult to predict and prevent, one is obliged to rely more heavily on precautions designed to minimize the impact of an occurrence of a natural disaster, such as emergency planning.

Plant personnel should always be aware of the special climactic, geological, and topographic conditions that exist in the area, since specific accident control programs will vary according to these conditions. In addition, plant personnel should be cognizant of accidents that can follow a natural disaster. For example, floods can cause pipelines to fail, lightning can start storage tank fires, hurricanes can cause power outages, prevailing winds can cause the rapid spread of fires and toxic releases, and tsunamis can cause a nuclear accident as witnessed in Japan in 2011.

Other natural disasters and “external events” are listed in Table 13.1, along with an abbreviated comment. Several of these topics are addressed in Part IV.

TABLE 13.1

Examples of Natural Disasters and “External Events”

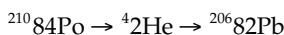
Disaster/Event	Comments
Aircraft impact	Sites less than 3 miles from airport have higher frequencies
Drought	May impact the availability of cooling water for a plant site
Earthquake	Damage to foundations of structures and equipment
External flooding	May impact storm water drainage impacts
Extreme winds	Can create large numbers of “missiles”
Extreme summer temperature	Will impact on the vapor pressure of chemicals in storage systems
Extreme winter temperature	Thermal stresses and embrittlement may occur in storage tanks
Fog	May increase frequency of accidents
Forest fire	Review location of plant relative to large areas of standing trees
Frost	Frost heave may damage foundations of plant structures
Ice cover	Ice blockage of rivers, loss of cooling, and mechanical damage due to falling ice are possible
Intense precipitation	Flooding effects need to be considered
Landslide	Can be excluded for most but not all sites in the United States
Lightning	Should be considered during design since computer control systems are vulnerable; may also damage plant power grid
Low lake or river level	May halt raw material and product shipping; alternative truck or rail shipping may be used
Meteorite impact	All sites have approximately same frequency of occurrence
Missile impact	Shrapnel and large pieces of pressure vessels are possible from explosions; rocks, bolts, and lumber may become missiles as a result of extreme winds caused by the explosion
Sabotage	Disgruntled employee may deliberately damage or destroy vital plant systems
Sandstorm	May damage equipment and block air intakes
Ship wreck	May halt raw material and production shipping; alternative truck or rail shipping may be used
Snow	Review design load of roofs; may increase frequency of in-plant accidents
Terrorist attack	High explosives and weapons may be used against selected targets; essential personnel may be held for ransom or killed
Transportation accidents	Site specific; accident on a major highway may cause evacuation of plant site
Tsunami	Site specific; series of damaging waves in coastal areas can cause flooding
Volcanic activity	May cause extensive downstream flooding; volcanic ash may damage equipment and plug air intakes; air space for planes may be compromised
War	Damage caused by high intensity combat will probably be greater than that caused by a worst credible case from a plant site

Illustrative Example 13.5

Describe radioactive transformations as they apply to alpha particles [10].

Solution

Alpha particle radioactive transformations are best described by the following example:



This is a useful example because the lead daughter product is stable and will not decay further. The neutron-to-proton ratio change from 1.5 to 1.51 is just enough to result in a stable element. Alpha particles are known as having a high linear energy transfer (LET). The alpha particles will only travel a short distance before losing their energy. A piece of paper or the top layer of skin will stop an alpha particle. Although alpha particles are not external hazards, they can be extremely hazardous if inhaled or ingested.

Illustrative Example 13.6

Hot equipment surfaces can lead to serious health-related problems. Describe a procedure that could be used to reduce this health hazard.

Solution

Hot surfaces can produce serious burns to personnel involved with chemical plant operations. Surfaces that are within reach of personnel should be insulated or the areas shielded to prevent accidental contact. Many critical areas in chemical plant operations should be restricted to all but experienced workers.

Illustrative Example 13.7

Briefly describe factors that should be considered in an accident arising from an airplane crash.

Solution

The incidence of aircraft impacts may be significantly higher in certain areas (e.g., in the vicinity of airports) than in others. An aircraft crash hazard is site specific and the severity of the accident resulting from a crash is strongly dependent on the kinetic energy of the aircraft. Two types of data are needed to analyze for aircraft crash hazards: the aircraft crash rate in the site vicinity (per unit area per year) and the effective target area that is vulnerable. Crash rates for different categories of aircraft can be obtained from state and national authorities (e.g., the FAA). The proximity of the site to airfields must be taken into account because crashes have a higher frequency within a radius of approximately 3 miles relative to locations outside this 3 mile radius.

Illustrative Example 13.8

List several procedures that can be instituted at a plant to reduce the possibility of a personal electrical accident.

Solution

1. Individuals should immediately report any unsafe electrical conditions to prevent an accidental shock.
2. Damaged or unauthorized extension cords must be taken out of service immediately.
3. Individuals must shut off power at the breaker before disconnecting a damaged cord.
4. To ensure that someone does not use equipment with a damaged power cord, the plug can be clipped off with a pair of wire cutters.
5. Experienced personnel must do all electrical work.
6. Equipment to be repaired should be tagged out and repairs verified before reuse.

13.4 Fires, Explosions, Toxic Emissions, and Hazardous Spills

This section provides information on physical properties of materials (flash points, upper and lower explosive limits, etc.) and methods to calculate the conditions that approach or are conducive to hazardous levels. Fire fundamental and hazards in industrial plants are covered first. The next three sections focus on accidental explosions. The last two sections address toxic emissions and hazardous spills, respectively. These latter types of accidents frequently result in fires and explosions; they can cause deaths, serious injuries, and financial losses.

13.4.1 Fire Fundamentals

By definition, fire is the combining of oxygen and fuel in proper proportions and at the proper temperature to sustain combustion. Combustion is the process in which a substance chemically reacts with fuel and oxygen at a rapid rate, producing light and heat. To produce combustion, four conditions must coexist:

1. Presence of fuel
2. Presence of oxygen
3. Heat
4. Mixing

If one of these conditions is missing, combustion may not take place, and if one condition is altered during combustion, the fire may become extinguished.

The growth and spread of fires occurs through heat transfer or the migration of burning materials. There are three main modes of heat transfer: *conduction*, *convection*, and *radiation*. *Conduction* is important particularly in allowing heat to pass through a solid barrier, causing ignition of material on the other side. However, most of the heat transfer from fires is by convection and radiation. *Convection* is the process by which heat is transferred by the motion of the heated matter, such as the flow of water through a hot pipe or a current of hot air. In *radiation*, heat travels in the same fashion as light is propagated—as a wave moving in all directions in straight lines until it is absorbed or reflected by another object [14,18].

Determining the fire potential of a fuel is best accomplished through an evaluation of the fuel's flammability characteristics. No single factor, however, defines a substance's flammability. When a flammability comparison is to be made among different substances, the following factors should be considered:

1. Flammability limits
2. Flash point
3. Burning velocity
4. Ignition energy
5. Autoignition temperature (AIT)

Each of these factors is discussed below.

Flammability limits (or explosion limits) for a flammable gas define the concentration range of a fuel–air mixture within which an ignition source can start a self-propagating reaction. The minimum and maximum fuel concentrations in air that will produce a self-sustaining reaction under given conditions are called the *lower flammability limit* (LFL) and the *upper flammability limit* (UFL). (The abbreviations LEL and UEL, for *lower* and *upper explosivity limits*, are sometimes used). The flammability limits are functions of [1]:

1. Ignition energy
2. Ignition pressure
3. Ignition temperature of the mixture or substance
4. Inert gas concentration
5. Relative humidity of the mixture or substance

The range of the flammability limits becomes greater when the ignition energy is higher, moving the UFL to a higher concentration. The flammability limits also increase when the initial pressure and/or initial temperature at which the ignition source is activated increases. In addition, the increase in pressure and temperature will increase the rate at which a flame propagates

through a gas [3]. Flammability limits can be significantly altered by changing the oxygen content or adding an inert gas to the fuel–air mixture. The heat capacity of the diluent, or inert gas, plays a role in flammability because the diluent will act as a heat sink. Thus, carbon dioxide is a better diluent than nitrogen because it has a higher heat capacity. The flammability limits also increase for drier mixtures. Table 13.2 shows the flammability

TABLE 13.2

Flammability Limits of Flammable Compounds
under Normal Pressure and Room Temperature

Compound	Limits of Flammability	
	Lower (% v/v)	Upper (% v/v)
Acetaldehyde	4.1	55.0
Acetone	3.0	11.0
Acetylene	2.5	81.0
Ammonia	15.0	28.0
Benzene	1.4	7.1
<i>n</i> -Butane	1.9	8.5
<i>i</i> -Butane	1.8	8.4
1-Butene	1.6	9.3
Carbon monoxide	12.5	74.0
Cyclohexane	1.3	8.0
Ethane	3.0	12.5
Ethyl alcohol	4.3	19.0
Ethylene	3.1	32.0
Ethylene oxide	3.0	80.0
Gasoline (100 octane)	1.4	7.6
Heptane	1.2	6.7
Hexane	1.2	7.5
Hydrogen	4.0	75.0
Methane	5.3	14.0
Methanol	7.3	36.0
Methyl ethyl ketone	1.8	10.0
Naphthalene	0.9	5.9
<i>n</i> -Pentane	1.5	7.8
Propane	2.2	9.5
Propylene	2.4	10.3
Isopropyl alcohol	2.0	12.0
Toluene	1.4	6.7
Vinyl chloride	4.0	22.0

Source: Coward, H.F. and G.W. Jones, *Limits of Flammability of Gases and Vapors*, Bureau of Mines, Bulletin 503, US Government Printing Office, Washington, DC, pp. 130–134, 1952.

limits of some flammable gases [19]. The flammability of a gas mixture can be calculated by using Le Chatelier's law given the flammability of the gas components as [1]:

$$LFL(\text{mix}) = \frac{1}{(f_1/LFL_1) + (f_2/LFL_2) + \dots + (f_n/LFL_n)} \quad (13.1)$$

$$UFL(\text{mix}) = \frac{1}{(f_1/UFL_1) + (f_2/UFL_2) + \dots + (f_n/UFL_n)} \quad (13.2)$$

where

f_1, f_2, \dots, f_n is the volume or mole fraction of each of the n components
 $LFL(\text{mix})$ and $UFL(\text{mix})$ are mixture lower and upper flammability limits, volume or mole fraction
 $LFL_1, LFL_2, \dots, LFL_n$ are the component lower flammability limits, volume or mole fraction
 $UFL_1, UFL_2, \dots, UFL_n$ are component upper flammability limits, volume or mole fraction

If data are not available for a particular gas mixture, it is possible to estimate a flammability limit by using data for a similar material and applying Equation 13.3 [1]:

$$LFL_A = \left(\frac{M_B}{M_A} \right) LFL_B \quad (13.3)$$

where M_A and M_B are the relevant molecular weights of components A and B , respectively. In addition, the LFL concentration can be estimated by assuming it is 1/2 the stoichiometric air required for combustion. For example, one can show that the stoichiometric combustion concentration of methane in air is 9.4%, which compares favorably, with the experimental value of 5.3% for methane's LFL. However, this estimation process only generally applies to hydrocarbons and does not apply well to other classes of combustion gases.

The *flash point* of a flammable liquid is defined as the temperature at which the vapor pressure of the liquid is the same as the vapor pressure corresponding to the LFL concentration of the material. The three major methods of measuring the flash point are [1]:

1. The Cleveland open-cup method
2. The Penskey–Martens closed-cup tester
3. The tag closed-cup method

When ignited, a flammable gas mixture of fixed pressure, temperature, and composition will propagate a combustion wave at a constant rate. The propagation mechanism is quite complex, but the interaction of these mechanisms is indicated by an observable burning velocity. *Burning velocity* is the velocity of the flame relative to the motion of the unburned gas or gas mixture. This measurable quantity is an excellent index of the energetic state of the combustion reaction. The burning velocity is a function of the gas mixture composition, pressure, and temperature. As one might suppose, the maximum velocity is observed at the stoichiometric concentration of the mixture.

A flammable fuel–air mixture can be ignited by a local source of ignition (flame, spark, hot gas, compression, shock wave, adiabatic heating, etc.), provided the local source possesses the *minimum ignition energy*, i.e., the ignition energy required to raise the temperature of the fuel–air mixture above the threshold temperature and to initiate a reaction. Ignition energy is a function of a flammable mixture’s composition. The minimum ignition energy is usually measured at the stoichiometric composition of the mixture.

The maximum spontaneous ignition temperature (SIT) or AIT is defined as the minimum temperature at which combustion occurs in a bulk gas mixture when the temperature of a flammable fuel–air mixture is raised in a uniformly heated apparatus. The AIT represents a threshold below which chemicals and combustibles can be handled safely.

An important factor in assessing the causes and effects of fires is the behavior of a fire’s flame. Knowledge of a flame’s spreading rate and heat intensity can reduce fire hazard potentials and fire damage. The classifications of flame behavior are:

1. Orifice flames
2. Pool flames
3. Jet flames
4. Fireball flames
5. Flash fire flames

Details of these flame types are available in Ref. [1,3]. In addition to assessing a fire’s flame characteristics to determine the cause and effect of a fire, knowledge of the fire accident type will provide insight into its potential ignition source and possible fire protection and prevention methods. Electrical, chemical, and metal fires can occur in a solid, liquid, or gaseous phase, and a discussion of these fires and their ignition sources follows.

13.4.2 Plant Fires

Having discussed the fundamental characteristics of fires in general, along with the different types of fires, one may now examine more closely fire accidents that occur in process plants. Specifically, plant fire classifications,

sources, causes, damage potentials, and detection and protection systems are reviewed.

The National Fire Protection Association (NFPA) recognizes four general classifications of fires [18].

1. *Class A fires.* Class A fires, which occur in highly flammable solid materials such as wood, cellulose, paper, and excelsior, are extinguished by bringing the burning materials below their ignition temperatures with the quenching and cooling effects of water. Under certain circumstances, these fires may be extinguished by the blanketing or smothering effects of dry chemical and carbon dioxide fire extinguishers.
2. *Class B fires.* Class B fires are those that occur in the vapor–air mixture overlying the surface of flammable liquids such as oil, greases, alcohols, kerosene, and gasoline. Class B fires are most successfully extinguished by limiting the air that supports combustion. Fire extinguishers, dispersing of dry chemicals, carbon dioxide, foam, halogenated hydrocarbon agents, and fog streams of water are recommended for Class B fires.
3. *Class C fires.* Class C fires involve electrical equipment. The extinguishing agents recommended for these fires are dry chemicals, carbon dioxide, compressed gas, and vaporizing liquids.
4. *Class D fires.* The last classification is reserved for fires occurring in combustible metals such as magnesium, lithium, sodium, and aluminum. Class D fires require special extinguishing methods and agents, such as the graphite-based type.

Industrial plants contain a great number of possible ignition sources. A study made by the Factory Mutual Engineering Corporation of almost 25,000 industrial fires reported over a decade ago indicates that, for the majority of fires, the ignition sources can be traced to the following general origins [20]:

1. Electrical (23%)
2. Smoking (18%)
3. Friction (10%)
4. Overheated materials (8%)
5. Hot surfaces (7%)
6. Burner flames (7%)
7. Combustion sparks (5%)
8. Spontaneous ignition (4%)
9. Cutting and welding (4%)
10. Exposure (3%)

11. Incendiarism (3%)
12. Mechanical sparks (2%)
13. Molten substances (2%)
14. Chemical action (1%)
15. Static electricity (1%)
16. Lightning (1%)
17. Miscellaneous (1%)

Details of the characteristics and modes of action of these ignition sources are available in Refs. [1,3,20]. These ignition sources cannot be eliminated, but they can be controlled by careful layout of the plant, proper design and maintenance of equipment, and the use of safety systems.

13.4.3 Causes of Plant Fires

The most common cause of fire accidents in process plants is equipment failure. This is primarily a result of poor equipment maintenance or poor equipment layout and design. Maintenance performed according to a detailed and well-structured schedule will significantly reduce the occurrence of these fire accidents. The second largest cause of fire accidents is ignorance of the properties of a specific chemical or chemical process. Proper training of employees will increase their knowledge of the properties of a specific chemical and chemical process, and can prevent many of these chemical fire accidents.

Leaks and spills resulting from an equipment failure will frequently cause fires. Large leaks can occur when a vessel, pipe, or pump fails; failure of a pump seal, pipe flange, or bore connection will cause a somewhat smaller leak. Since fires at pumps and/or at flanges are possible, it is essential to assess the effect of such fires on the equipment above or near the pump or flange. Incidence of pump fires can be minimized by using double mechanical seals in all at-risk pumps. Pipe flanges also can be protected against fires by placing an insulating pad between the joint ring and pipe bore, and by specifying more massive flanges to minimize the temperature gradient across the flange.

Thermal insulation (or lagging) on plant equipment may become soaked or impregnated with oils and other flammable liquids. When the lagging gets hot, spontaneous combustion can occur. Lagging fires are affected by oil leaks, insulation material, and temperature. Spontaneous combustion occurs only when the oil is nonvolatile since volatile oil evaporates more easily, thus delaying the accumulation of oil that can reach its AIT. A continuous leak may actually inhibit lagging fires since the lagging fire can be oversaturated and not be able to ignite. A good insulating material with a low thermal conductivity is favored by the lagging fire. A low density, porous structure provides surface area for the air to diffuse in. A thick lagging gives good insulation; therefore, spontaneous combustion is more likely to occur

on a thicker lagging. To prevent lagging fires, the following precautions are recommended:

1. Prevent leaks
2. Use appropriate sealings (cement finish or aluminum foil)
3. Use special insulation materials such as foam glass or crimped aluminum sheeting

The best way to fight a fire is to remove any one of three essential conditions required to sustain the fire:

1. The fuel source (e.g., by eliminating the leaks in a process plant)
2. Heat (e.g., by dousing a fire with water)
3. The supply of oxygen (e.g., by applying foams or inert gases)

Various fire extinguishing systems can be used. Typical systems include:

1. Water systems
2. Foam systems
3. Carbon dioxide systems: often used on Class B fires
4. Dry chemical systems (e.g., sodium bicarbonate)
5. Water spray systems
6. Steam jet systems

13.4.4 Explosion Fundamentals

An *explosion* is defined by Strehlow and Baker [21] as an event in which energy is released over a sufficiently small period of time and in a sufficiently small volume to generate a pressure wave of finite amplitude traveling away from the source. This energy may have been originally stored in the system as chemical, nuclear, electrical, or pressure energy. However, the release is not considered to be explosive unless it is rapid and concentrated enough to produce a pressure wave that can be heard.

Many types of processes can lead to explosions in the atmosphere. They may cause accidental explosions such as condensed phase explosions with or without confinement (liquids), combustion explosions in enclosures (gases and dusts), explosions in pressure vessels, BLEVEs, and UVCEs. There also are intentional explosions such as nuclear weapon explosions, condensed phase high explosions, vapor phase high explosions, gunpowder propellant explosions, and explosions due to natural phenomena such as lightning, volcanic eruptions, and meteor landings. This section focuses mainly on the fundamentals of accidental explosions.

To understand the basis or fundamental principles and characteristics of explosions, certain terms must be defined. This discussion begins by reviewing explosion (or flammability) limits, as covered in the preceding section. An explosion limit is the concentration range of a flammable or explosive fuel–air mixture within which an ignition source can start a self-propagating reaction. The two ends or limits of this concentration range (as noted earlier) are known as the *lower explosion limit* (LEL or LFL) and the *upper explosion limit* (UEL or UFL). For dust–air mixtures, the lower and upper explosion limits can be determined by calculations if the chemical nature and heat of combustion of the dust are known. Typical ranges for industrial dust are from 20 to 60 g/m³ for the LEL and between 2000 and 6000 g/m³ for the UEL.

An *explosion pressure*, P_{ex} is the pressure in excess of the initial pressure at which the explosive mixture is ignited. The rate of pressure rise is represented by dP/dt , a pressure change with respect to time. This is a measure of the speed of the flame propagation, hence of the violence of the explosion. Typical values of maximum explosion pressures in a closed vessel range from 7 to 8 bars. The rate of pressure rise can vary considerably with the flammable gas. The influence of vessel volume on the maximum rate of pressure rise for a given flammable gas is characterized by the cubic law as

$$\left(\frac{dP}{dt} \right)_{\max} V^{1/3} = K_G = \text{constant} \quad (13.4)$$

where

V is the vessel volume, m³

K_G is the constant, bar-m/s

$(dP/dt)_{\max}$ is the maximum pressure rise, bar/s

The cubic law may be applied only to systems that are similar with respect to vessel shape, degree of turbulence, ignition source, and concentration of the gas–air mixture [20]. Table 13.3 provides K_G values of some flammable gases obtained by using spark gap ignition with an ignition energy of 10J. A similar cubic law equation (Equation 13.5) applies for dust explosions in closed vessels. Table 13.4 gives K_{St} values for fine dusts [20]:

$$\left(\frac{dP}{dt} \right)_{\max} V^{1/3} = K_{St} \quad \text{for } V > 0.04 \text{ m}^3 \quad (13.5)$$

where K_{St} is the constant, bar-m/s.

The explosion of a flammable mixture in a vessel or enclosure can be either a *deflagration* or a *detonation*. A deflagration is an explosion that occurs when:

TABLE 13.3

Average K_G Value of Gases, Ignited at Zero Turbulence

Flammable Gas	K_G (bar-m/s)
Methane	55
Propane	100
Hydrogen	550

Source: Reproduced with permission from NFPA 68-2007, *Standard on Explosion Protection by Deflagration Venting*, Copyright © 2007, National Fire Protection Association. This reprinted material is not the complete and official position of the NFPA on the referenced subject, which is represented only by the standard in its entirety.

TABLE 13.4

K_{St} Values of Technical Fine Dusts: High Ignition Energy

Type of Dust	P_{max} (bar)	K_{St} (bar-m/s)
PVC	7.6	46
Milk powder	5.8–8.8	28–125
Polyethylene	8.0	156
Sugar	8.5	138
Epoxy resin dust	7.9	129
Brown coal	9.2	129
Wood dust	10.5	205
Cellulose	9.7	229
Urea-formaldehyde resin	10.2	136
Aluminum	12.4	415

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1. The concentration of the flammable mixture is within the flammability range
2. There is a source of ignition
3. The mixture is above its AIT

In other words, deflagrations are the result of a combustion reaction with a self-propagating flame front. These reactions occur with a low rate of pressure rise and a low peak pressure fall. A detonation occurs at similar conditions except that the mixture composition is limited to a narrower range than that for an explosion.

The maximum explosion pressure is a function of the initial pressure, P . If the initial pressure is increased by a factor of 2, the maximum explosion pressure and the maximum pressure rise will also increase by a factor of about 2 for both flammable gas and dust mixtures. When the initial pressure is less than 10 mbar, it is usually no longer possible to have an explosion.

An explosion in air is a process by which a pressure wave of finite amplitude is generated in air by a rapid release of energy and is accompanied by a sudden or instantaneous rise in pressure, and by the formation of shock waves or blast waves. As a blast wave passes through the air, rapid changes in density, temperature, and particle velocity are also encountered. The blast wave then generates overpressure that applies stresses to any nearby structures. This load results in such adverse effects as damage to buildings and/or equipment and human injury or death.

The shape of the pressure profile near the center of the explosion depends on the type of explosion. At some distance from the explosion center, the region of positive pressure (or overpressure) in the shock wave is followed by a region of negative pressure (or underpressure). The underpressure is usually very weak, seldom exceeding 4 psi [20]. Other properties of the blast wave are the *shock velocity*, which is the rate or speed of the blast wave as it travels through the air, the *particle velocity* (or *peak wind velocity*), the *peak dynamic pressure*, and the *peak rejected overpressure*.

Confined combustion explosions (gaseous or liquid) usually occur when a flammable vapor leaks into an enclosure and mixes with air to form a flammable mixture, whereupon this mixture contacts an ignition source that was present before the leak occurred. This type of explosion can also occur in storage tanks or ships or planes where the vapor space above the stored flammable liquid (fuel) is in the explosive range. In this case, an ignition source accidentally introduced will cause an explosion.

Confined dust explosions occur primarily in coal mines, grain elevators, feed silos, boilers, and chemical plants. Coal mine explosions have been occurring since the dawn of the Industrial Revolution. Explosions in mines are normally started by the ignition of a pocket of methane. Larger dust explosions occur as the layered dust is picked up by a primary explosion and triggers a disastrous secondary explosion. Dust explosions in the chemical and

pharmaceutical industries are generally confined to process equipment since dust control techniques are sophisticated in modern production facilities.

The handling of solids is becoming more important because the production of solids is increasing as a function of time. For example, there is a significant industrial emphasis to produce agricultural products as powders instead of liquids and to use powdered paints to reduce hydrocarbon emissions. The processing of grain is also increasing because of the added needs of the food industry to meet the world's population growth. These added uses/application of solids will increase the potential for dust explosions.

13.4.5 Unconfined Vapor Cloud Explosions (UVCEs)

An UVCE is one of the most serious hazards in the process industry. Not only is an UVCE large and destructive, but it may occur at some distance away from the vapor release source. Thus, its zone of influence can span a large area. Vapor clouds are usually caused by vessel failures, failures of piping, valves, or fittings, and releases from venting facilities. The material escaping may be a gas, a volatile liquid, a superheated liquid, or a refrigerated liquid. Flashing superheated liquids tend to cause the largest vapor clouds.

The distance traveled by a cloud of flammable vapor is site specific and relies on several dispersion factors, which are discussed in Chapter 10. It is not likely that a vapor cloud would travel far in any industrial or urban area. In open areas with few sources of ignition, a vapor cloud may drift several miles. The time before ignition can range from 10 s to 15 min.

Accidental explosions are potentially the most dangerous since they are a major concern for any industrial plant that deals with either pressurized or flammable gases. An accidental explosion occurs not by design and therefore is not similar to an intentional explosion where the conditions are planned and can be controlled. Accidental explosions usually are the result of equipment failure or operator error. Although accidental explosions are by definition unforeseen events, the procedures discussed in the next chapter may be implemented either to minimize their effects or to prevent them entirely. A *natural* explosion is also an uncontrolled and unexpected event. However, unlike an accidental explosion, it cannot be prevented. Some examples of natural explosions include lightning and volcanic eruptions. Under the right critical conditions, natural explosions also trigger and cause accidental explosions.

An *intentional* explosion usually has no undesired effects because it is normally controlled and limited to an isolated area. Examples include explosions from explosive weapons, blasting lasers, gun powder blasts, and contained explosions.

13.4.6 Plant Explosions

The previous section presented three major types of explosion. This section more closely examines plant-related explosions, focusing on causes, results,

and damage potential. The means for explosion protection and prevention are the subject of a subsequent chapter.

Many factors may lead or contribute to a plant explosion. However, plant explosions most often encountered in industry are caused either by faulty operational procedures or by faulty equipment. Several of the more common types of plant explosions include chemical, nuclear, expanding vapors, and pressurized gas explosions.

A *chemical explosion* tends to have a slower pressure buildup compared with accidents of other types; its most likely cause is a runaway chemical reaction. Such an unstable and potentially dangerous situation can result from the combination of two or more incompatible chemicals, or the improper storage of potentially explosive or highly reactive chemicals. A runaway, or uncontrolled, reaction usually is exothermic and due to a system upset (e.g., presence of excess catalyst and/or reactants or inadequate cooling or mixing); which permits the pressure to build up to high enough levels to cause vessel rupture. This type of explosion tends to occur when the contents of the reactor are gaseous. However, if the contents are liquid and the temperature is above the flash evaporation temperature, the result is called a BLEVE, referred to earlier and described in more detail later.

The most serious accident that can occur in a nuclear plant is a *reactor core meltdown*. In a core meltdown, the enclosed gases physically melt through the reactor vessel, and once contacted with cooler liquids or vapors either in a cooling jacket or in the outer environment, cause a physical explosion to occur. However, the hazard caused by the explosion itself is minimal and more localized compared with the release of radioactive material that accompanies such an accident.

A BLEVE occurs when a pressure vessel containing a liquid is heated to a temperature high enough to cause the metal to lose strength and rupture. The source of the heat is normally another fire near the vessel. The effects of a BLEVE depend on whether the liquid in the vessel is flammable or not. If the liquid is flammable, it may either cause a fire, which radiates heat, or form a vapor cloud, which could result in a second explosion.

Compressed air lines are very susceptible to a combustion-generated explosion, fueled by oil or char on the pipe walls. Explosions in pipelines can cause considerable damage. Pipelines within which gas, vapor, or dust explosions can occur must be designed to have sufficient mechanical strength to withstand pressure or stress more above that required simply to contain the fluid during transfer.

About two-thirds of the historical major chemical plant losses have involved explosions. Explosions can be prevented or controlled. The release of energy is so rapid that the usual concepts of extinguishment are practically impossible to apply. It is essential during the risk evaluation procedure to identify those processes, operations, and plant areas that are susceptible to explosion hazards. Anticipating the type and degree of the explosion hazard well in advance of a hazard event is essential if the proper explosion prevention steps are to be taken.

Explosions are likely to occur whenever circumstances are favorable as a result of a variety of basic conditions:

1. Rapid release of energy through the ignition of atmospheric mixtures of flammable gases, vapors, or combustible dusts within the explosive range
2. Rapid release of energy through deflagration or detonation of unstable chemicals after exposure to an initiating force or energy
3. Rapid release of energy through decomposition or exothermic chemical reactions
4. Rapid release of energy through the mechanical failure of a pressure container as a result of mechanical defect or the generation of excessive pressure

The magnitude of an explosion not only depends on the quantity and nature of the materials involved but also on process or operating conditions, degree of confinement, temperature, pressure, type of equipment, nature of operation (outdoor or closed construction), and prevention or control measures applied.

Prevention and control essentially deals with the elimination of those conditions that make the explosion possible. This is accomplished through the application of basic safety standards, acceptable safe practices, and good engineering judgment. Primary standards and safe practices applicable under the various explosion categories are available in Ref. [22,23]. Explosion protection (control) may be accomplished with one or a combination of the following:

1. Containment
2. Flame barriers
3. Explosion suppression
4. Relief venting
5. Quenching

In conclusion, to prevent accidents due to fires and explosions, engineers and scientists must be familiar with

1. The fire and explosion properties of materials
2. The nature of the fire and the explosion process
3. Procedures to reduce fire and explosion hazards

Needless to say, training in this area would be extremely beneficial to the engineer or scientist working in or for the chemical process industry.

13.4.7 Toxic Emissions

The next two sections discuss accidents that result in the release of a toxic emission or a hazardous spill. In general, a toxic emission can be considered to be either continuous or instantaneous. Only the atmospheric effects of toxic emissions are considered in this section. However, hazardous spills (next section) usually imply a liquid contamination of either soil or water systems. In addition, a hazardous chemical spill may lead to a release of toxic emissions.

Continuous releases usually involve low levels of toxic emissions which are regularly monitored and/or controlled. Such releases include continuous stack emissions and open or aerated chemical processes in which certain volatile compounds are allowed to be released into the atmosphere through aeration or agitation. Mathematical models for these releases to the environment are covered in detail in Chapter 10.

Greater concern is warranted for the case of an instantaneous release, which is usually the result of an uncontrolled process. Most of these incidents are the result of a highway or railway accident or a fire, windstorm, or other natural accident. However, the cause can sometimes be linked to the breakdown of normal safeguards in plants, factories, mines, or chemical storage facilities. Whatever the cause, the result is often a significant potential threat to life, property, and/or the environment. The accident at Bhopal described in Part I is an excellent example of an instantaneous release in which a chemical process malfunction seems to have led to an uncontrolled toxic release. A release is said to be “instantaneous” if a significant amount of hazardous or toxic material is emitted over a short period of time. Since the disaster at Bhopal, chemical process industries have implemented certain risk-reducing measures that have cost billions of dollars. These measures are aimed at a tighter, safer control of chemical processes that produce or use hazardous substances. The measures include improving the storage and processing of hazardous chemicals, substituting benign compounds for hazardous ones in the manufacturing process, and producing certain hazardous substances under more controlled conditions.

The release/emission/discharge from a pipe or a vessel can be described mathematically. *Perry's Chemical Engineers' Handbook* [24] has done an excellent job in presenting key predictive equations for a gas, a liquid, or a mixed phase release. Both gas and liquid discharges are included here since an emission usually consists of a (volatile) flashing liquid and vapor plus non-condensable gases and (possibly) some solid particulates. In addition, the discharge flow may be sonic and/or transient (varies with time). Note that some of these equations apply to the next section, which is concerned with hazardous spills. The following detailed information is provided in *Perry's Chemical Engineers' Handbook* [24]:

1. Discharge flow regime
2. General two-phase flow relationships

3. Two-phase orifice discharge
4. Subcooled liquid orifice discharge
5. Compressed fluid orifice discharge
6. Choked two-phase flow
7. Full-bore and punctured pipe discharge
8. Two-phase pipe discharge
9. Subcooled liquid inclined pipe discharge
10. Inclined pipe discharge
11. Horizontal pipe discharge
12. Discharge coefficients
13. Blowdown modeling

The Center for Chemical Process Safety (CCPS) of the American Institute of Chemical Engineers has done a commendable job of extracting some of the key equations applicable to a toxic gas emission and the reader is referred to their document [25] for further details.

13.4.8 Hazardous Spills

Hazardous wastes are legally defined as those that may cause adverse or chronic effects on human health or the environment when not properly controlled. Hazardous wastes are generated either because processes have converted harmless materials into hazardous substances or because naturally hazardous materials have been concentrated and released into the environment. These substances may be ignitable, reactive, corrosive, radioactive, infectious, or toxic. They may exist as solids, liquids, sludges, powders, or slurries. About 90% of them are liquid or semiliquid. Some of these wastes are nondegradable and may persist in nature indefinitely.

Hazardous chemical spills may have adverse effects on natural water systems, the land environment, and whole ecosystems, as well as the atmosphere. Major spills evolve from accidents (see also Chapter 6) that somehow damage or rupture vessels, tank cars, or piping used to store, ship, or transport hazardous materials. In such cases, the spills must be contained, cleaned up, and removed as quickly and effectively as possible to minimize damage to human health and the surrounding environment.

Spills of hazardous materials from transport vehicles pose one of the most significant problems in accidental contamination of the aquatic ecosystem, with its associated danger and threat to public health and welfare. In accidents involving land transportation, once a leak or spill has been contained, immediate cleanup must ensue and the spilled material must be excavated and disposed of properly. A quick response time is necessary to collect

spilled materials before they are able to breach dikes, be absorbed into the ground, or otherwise flood the environment.

Hazardous wastes can be classified under five general categories:

1. Chlorinated and nonchlorinated waste oils
2. Flammable wastes and synthetic organics
3. Toxic metals, etchants, and pickling and plating wastes
4. Explosive, reactive metals and other compounds
5. Salts, acids, and bases

A particular waste may overlap any number of these five categories. Flammable wastes are comprised mainly of contaminated solvents; this category also includes many oils, pesticides, plasticizers, complex organic sludges, and off-specification chemicals. Synthetic organic compounds include halogenated hydrocarbon pesticides, polychlorinated biphenyls, and phenols.

As indicated in the previous section, information on liquid emissions for a variety of conditions is available in the literature, including equations for two-phase flow [23,24]. Key equations for liquid and two-phase discharges have also been provided by CCPS [25].

Illustrative Example 13.9

Calculate the UFL and LFL of a gas mixture that consists of 30% methane, 50% ethane, and 20% pentane by volume.

Solution

Using Equations 13.1 and 13.2 and Table 13.2,

$$\begin{aligned} LFL(\text{mix}) &= \frac{1}{(f_m / LFL_m) + (f_e / LFL_e) + (f_p / LFL_p)} \\ &= \frac{1}{(0.3/0.053) + (0.5/0.03) + (0.2/0.015)} \\ LFL(\text{mix}) &= 0.028 = 2.8 \text{ vol}\% \end{aligned}$$

$$\begin{aligned} UFL(\text{mix}) &= \frac{1}{(f_m / UFL_m) + (f_e / UFL_e) + (f_p / UFL_p)} \\ &= \frac{1}{(0.3/0.14) + (0.5/0.125) + (0.2/0.078)} \\ UFL(\text{mix}) &= 0.115 = 11.5 \text{ vol}\% \end{aligned}$$

Illustrative Example 13.10

A flammable vapor flows through a 2 in. diameter insulated pipe at a flow rate of 4.5 acfm. A lagging fire started and heated a 4 ft length of the pipe to 150°F, which is above the ignition temperature of the vapor. The ignition delay time of the vapor is expressed by

$$\ln(t) = \left(\frac{250}{T} \right) + 0.5 \quad (13.6)$$

where

t is the ignition time delay, s

T is the absolute temperature, °R

Will ignition take place?

Solution

The ignition time delay can be calculated from Equation 13.6 as:

$$\ln(t) = \left[\frac{250}{(150 + 460)} \right] + 0.5 = 2.5 \text{ s}$$

The average residence time, t_r , of the vapor in the 4 ft section of pipe is:

$$t_r = \frac{\text{Pipe volume}}{\text{Volumetric flow rate}} = \left[\left(\frac{\pi(2 \text{ in.}/12 \text{ in./ft})^2}{4} \right) \left(\frac{4 \text{ ft}}{4.5 \text{ ft}^3/\text{min}} \right) \right]$$

$$t_r = \frac{0.087 \text{ ft}^3}{4.5 \text{ ft}^3/\text{min}} = 0.019 \text{ min} = 1.16 \text{ s}$$

The residence time of the vapor in the pipe section is less than the ignition delay time. Therefore, ignition will not take place.

Illustrative Example 13.11

A round vessel filled with hydrogen is ignited. The volume of the vessel is 0.5 m³. Calculate the maximum pressure rise. Also calculate the maximum pressure rise for the same vessel filled with methane. The K_G values for hydrogen and methane are 550 and 55 bar-m/s, respectively.

Solution

Equation 13.4 is employed to calculate the maximum pressure rise in an enclosed vessel as:

$$\left(\frac{dP}{dt}\right)_{\max} V^{1/3} = K_G \quad (13.4)$$

Rearranging Equation 13.4 allows one to solve for $(dP/dt)_{\max}$ as:

$$\left(\frac{dP}{dt}\right)_{\max} = \frac{K_G}{V^{1/3}}$$

Substituting for hydrogen yields:

$$\left(\frac{dP}{dt}\right)_{\max} = \frac{550 \text{ bar}\cdot\text{m/s}}{(0.5 \text{ m}^3)^{1/3}} = 693 \text{ bar/s}$$

The predicted maximum pressure rise for methane is:

$$\left(\frac{dP}{dt}\right)_{\max} = \frac{(55 \text{ bar}\cdot\text{m/s})}{(0.5 \text{ m}^3)^{1/3}} = 69.3 \text{ bar/s}$$

Illustrative Example 13.12

List the seven necessary ingredients for a dust explosion to occur [24].

Solution

The seven key factors are

1. Air (oxygen)
2. Fuel source (dust)
3. Mixing of these two ingredients
4. Low moisture
5. Minimum concentration
6. Ignition source
7. Enclosure

Note that one needs *all* of the aforementioned items for an explosion to occur. Thus, eliminating only one can prevent the explosion. Industries generally focus on designing controls for Items 5 through 7 plus training to help prevent dust explosions [24].

13.5 Hazard Event Evaluation Techniques

A number of hazard evaluation techniques have been developed over the years to help consistently and carefully identify potential hazards in chemical and manufacturing plants. When applied properly to a given system,

hidden system failure modes can be identified and techniques for their rectification can be recommended and implemented. Many occupational and environmental safety problems have been identified as the result of an emergency, and in many of these situations, once the emergency is over, the problem is considered resolved. Although solving safety problems once they have occurred is the domain of the design engineer, the true role of the design team must be to prevent accidents from occurring in the first place. Hazard evaluation techniques, when integrated with engineering design, provide the design engineer with the necessary tools to identify and modify those components of the system that have the potential to cause an accident, thus preventing accidents before they result in loss of life and/or property and environmental damage [26,27].

To properly apply system safety techniques to the design and operation of potentially hazardous technologies, the design engineer must have a clear understanding of the system and be able to prepare a written response to questions such as:

1. What is the intended function of the system?
2. What are the raw materials, intermediates, final products, and by-products?
3. What steps are taken to convert the raw materials to final products? (e.g., chemical reactions and physical operations)
4. How does the system interact with the environment? (e.g., hazardous waste streams and toxic releases)
5. How does the system interact with personnel? (e.g., the need for personal protective equipment [PPE])
6. What sources of energy does the system use and how is this energy supplied to the system?
7. What are the maintenance requirements of the system?
8. How does the system interact with other systems within the plant?

The aforementioned list is illustrative only and must be tailored or adjusted to the particular system design being evaluated.

Proper application of an event/hazard evaluation technique also requires a sound knowledge of the types of hazards involved within the system. The design engineer should develop a list summarizing the types of hazards that warrant further evaluation within the system. This list could take the following hazards into account:

1. Toxic chemicals
2. Fires
3. Explosions

4. Runaway chemical reactions
5. Temperature extremes or excursions
6. Pressure extremes or excursions
7. Equipment/instrumentation malfunction that can be a factor in the creation of a hazard
8. System moving parts
9. Electrical malfunctions
10. Hazardous noises and vibrations
11. Mechanical malfunctions
12. Environmentally damaging releases
13. Radiation exposures

After the system has been defined, a hazard evaluation technique can be used to identify different types of hazards that exist within the system components and to propose possible solutions to eliminate these hazards. This topic is treated in more detail in the next two chapters. These procedures are extremely useful in identifying system modes and failures that can contribute to the occurrence of accidents, and they should be an integral part of different phases of process development from conceptual design to installation, operation, and maintenance [23–27]. The hazard evaluation techniques that are useful in the preliminary and detailed stages of the design process are reviewed below, and include:

1. The system checklist approach
2. Safety review/safety audits
3. “What if” analyses
4. PHAs
5. HAZOP studies

Other hazard evaluation procedures appearing in the literature include:

1. Relative ranking techniques
2. Failure modes effects criticality analyses (FMECA)
3. Fault tree analyses (FTA)
4. Event tree analyses (ETA)
5. Cause–consequence analyses (C-CA)

However, these latter procedures are characterization topics more related to risk and deal with causes (Chapter 14) and consequence (Chapter 15) and consequently are treated elsewhere.

13.5.1 System Checklists

A system checklist is useful to identify compliance problems as well as those areas of the system that require further hazard evaluation. The method is easy to use and can be applied to any component of a given system such as equipment, instrumentation, materials, and procedures. The checklist essentially identifies common hazards in order to ensure compliance with previously applied standard procedures. It can be applied at the design, construction, startup, operation, and even shutdown phase(s) of a project or system. This method produces qualitative results but must be conducted by an engineer thoroughly experienced with the system being evaluated. Once the checklist is prepared, however, it can be used by engineers or managers who may have less technical experience with the system than the individual preparing the original checklist [27].

The method of checklists can also be applied to any phase of a project's life cycle from preliminary design to shipment of products and disposal of wastes. Since the safety requirements of a system are a strong function of the nature of the process, preparing a standard "checklist" format applicable to all systems may be difficult. Checklists must generally be streamlined to the specific problem at hand. For example, in a preliminary plant design, the design engineer might prepare a checklist to cover the following areas:

1. Raw materials
2. Products
3. Intermediate products
4. Equipment
5. Instrumentation
6. Plant layout
7. Startup
8. Shutdown
9. Emergency shutdown
10. PPE
11. Contingency planning (both personnel and community)
12. Waste disposal

Each specific area mentioned can be further expanded to provide more details for hazard evaluation. Although the results of a checklist study are qualitative, these results can be used to identify design areas that require further hazard evaluation and to communicate the safety needs of the plant to management.

As indicated earlier, these checklists may be used to indicate compliance with standard procedures. A checklist is easy to use and can be applied to each stage of a project or plant development and is a convenient means of

communicating the minimal acceptable level of hazard evaluation that is required for any job, regardless of scope. As such, it is particularly useful for an inexperienced engineer to work through the various requirements in the checklist to reach a satisfactory conclusion. However, to be valuable, a system checklist should be audited and updated regularly.

Interestingly, many companies use standard checklists for managing the development and execution of a project from initial design through plant shutdown. It serves as a form for approval by various staff and management personnel before a new or retrofit project can move ahead.

13.5.2 Safety Reviews/Safety Audits

Safety Reviews/Safety Audits essentially consist of a walk-through on-site inspection that can include interviews with plant staff to identify plant conditions or operating procedures that could lead to an accident. While this qualitative technique is most commonly applied to operating process plants, it is also applicable to smaller systems. The walk-through on-site inspection can vary from an informal, routine function that is principally visual, with emphasis on housekeeping, to a formal, extended duration examination by a team of inspectors with appropriate backgrounds and responsibilities. The emphasis in this section is on the latter and it is sometimes referred to as a Safety Review, a Process Safety Review, a Loss Prevention Review, or a Process Review. As described earlier, such a program is intended to identify plant operating conditions/procedures that could lead to an accident and significant losses of life or property.

This comprehensive review is intended to complement other safety efforts and routine visual inspections. The review includes interviews with many people in the plant including operators, maintenance staff, engineers, management, safety staff, and others, depending upon the plant organization. The review looks for both major and minor risk situations. General housekeeping and personnel attitudes are not the primary objectives, although they can be significant indicators of where to look for real problems or places where meaningful improvements are needed. Various hazard evaluation techniques, such as checklists (see previous section) and “what if” analyses (see next section), can also be used during the review.

At the end of the Safety Review/Safety Audit, recommendations are made for specific actions that are required including justifications, recommended responsibilities, and completion dates. A follow-up evaluation or reinspection is usually planned to verify the implementation and acceptability of the corrective action.

For a complete review, data requirements that the team will need include:

1. Access to applicable codes and standards
2. Detailed plant descriptions such as piping and instrumentation drawings and flowcharts

3. Plant procedures for startup, shutdown, normal operation, and emergencies
4. Personnel injury reports
5. Hazardous incidents reports
6. Maintenance records such as critical instrument checks, pressure relief valve tests, and pressure vessel inspections
7. Process material characteristics (e.g., toxicity and reactivity information)

13.5.3 “What If” Analyses

The main purpose of the “what if” qualitative method is to identify the hazards associated with a process by asking questions that start with “what if” [28]. This method can be extremely useful if the design team conducting the examination is experienced and knowledgeable about the operation. If not, the results are usually incomplete. The examination usually starts at the point of input of reactants and raw materials and continues in a “rail-road” manner according to the flow of the process [27–32].

The first step of a “what if” analysis is to define the study boundaries. There are two types of study boundaries to be considered: the consequence category boundary, which includes public risk, employee risk, and economic risk; and the physical boundary, which addresses the section of the plant that should be considered for analysis.

The second step is to obtain all the information about the process that will be needed for a thorough evaluation, including but not limited to the process materials used and their physical properties, the chemistry and thermodynamics of the process, a plant layout, and a description of all the equipment used, including controls and instrumentation. The last part of the information-gathering step may be viewed as the preliminary formation of the “what if” questions.

The third step is to select a review team. The team is usually composed of two or three members that have combined experience in the process to be studied, knowledge in the consequence field, and experience in general hazard evaluation. If the team is inexperienced, results may be incomplete or incorrect.

Once the team has been selected, the review is conducted. Starting with the process inputs and proceeding through the system to the outputs, each of the “what if” questions is addressed by identifying the hazard and its consequence and then recommending solutions or alternatives to alleviate the risk [28].

The “what if” approach uses questions that begin with “what if” such as:

1. “What if” the wrong material is delivered?
2. “What if” Pump A stops running during startup?

TABLE 13.5*“What If” Analysis of an Ethylene Polymerization Reactor*

What If ...	Consequence/Hazard	Recommendation
1. Cooling water pump breaks down	Runaway reaction/explosion/fire	Stand-by pump/alarm system
2. Too much oxygen fed into reactor	Runaway reaction/explosion/fire/flying debris	Alarm system/feed flow control/initiator flow control
3. Wrong initiator	None likely	NA
4. Valve after reactor gets clogged	Pressure buildup/explosion/fire/flying debris	Feed flow control/initiator flow control/alarm system
5. Compressor breaks down	None likely	NA
6. Trauma to cooling jacket	Runaway reaction/explosion/fire/flying debris	Temperature alarm/feed flow control

3. “What if” the operation fails to respond?

4. “What if” the operator opens Valve B instead of Valve A?

The final step in the “what if” analysis is reporting the results in a systematic and easily understood format. An example of a common format is provided in Table 13.5, which includes the questions, their consequences, and recommendations for resolving or eliminating these adverse effects. An ethylene polymerization process is used in Table 13.5 to demonstrate the format for a “what if” analysis and typical results when a range of hazards may result.

Although the “what if” procedure is not as structured as some other event/hazard identification studies, it is a powerful procedure if staff members are experienced and the correct “what if” questions are asked. Otherwise (and as indicated earlier), the results from the procedure may neither be complete nor accurate.

13.5.4 Preliminary Hazard Analyses (PHAs)

A PHA is an overall qualitative study that yields a rough assessment of the potential hazards and may also include the means for their rectification within a system. It is called “preliminary” because it is usually refined through additional studies and is designed to serve as a precursor to expanded studies. In effect, its purpose is to aid in recognizing problem areas early, thus saving time and money in the long term. It can provide a cost-effective, early-on plant method for hazard identification for cases where past experience provides little or no insight into any potential hazard problems. A PHA, which is part of the U.S. Military Standard System Safety Program, contains a brief description of potential hazards in system development, operation, or waste disposal. This method focuses special attention on sources of energy for the system and on hazardous materials used or generated that might adversely affect the system or environment. Resources necessary to conduct a PHA

include plant design criteria and equipment and material specifications that are reviewed by competent assessment team personnel.

The results of a PHA study can be summarized in the form of a table or a logic diagram. In either format, potential hazards that pose a high risk, along with their cause(s) and major effects, are identified. In addition, for each hazard identified, preliminary means of control are also often prescribed. Thus, a PHA is not only performed to develop a list of possible hazards but also is used to identify those hazardous features of a system that can result in unacceptable risks and to assist in developing preventive measures in the form of engineering or administrative controls or use of PPE to mitigate them [27,28,33,34].

13.5.5 Hazard and Operability (HAZOP) Studies

A HAZOP study is a systematic approach to recognizing and identifying possible hazards that may cause failure of a piece of equipment in new or existing facilities. In effect, it investigates potential HAZOP problems. A HAZOP study may be applied to operating process plants, or it may be performed at various stages throughout the design of a new facility or process. An early start will lead to a safer, more efficient design and, ultimately, lower risks and higher profits.

Before any action is taken, the goals and objectives of the study should be defined. There are generally six objectives identified for a HAZOP study:

1. To identify areas of the design that may possess a significant hazard potential
2. To identify and study features of the design that influence the probability of a hazardous incident occurring
3. To familiarize the study team with the design information available
4. To ensure that a systematic study is made of the areas of significant hazard potential
5. To identify pertinent design information not currently available to the team
6. To provide a mechanism for feedback of the study team's detailed comments to the client (if applicable) regarding process safety and operational complexity

Next, the method requires a determination of the plant limits, i.e., the areas of the plant that will be evaluated. Once plant limits are defined, a team consisting of technical experts in plant design and operations, plus other experts, as required, needs to be convened to conduct this qualitative enterprise. An experienced team of principal engineers, a HAZOP chairperson, and an external HAZOP expert is the recommended makeup of the foundation for the team. Other experts from other disciplines, such

as instrumentation and process control, may be periodically called on to identify and evaluate deviations from normal operations during the HAZOP study.

Before any assessment can be performed, the team must be supplied with required documentation and process details. As with other hazard identification steps, the following materials are usually needed:

1. Process description
2. Process flow sheets
3. Data on the chemical, physical, and toxicological properties of all raw materials, intermediates, and products
4. P&IDs
5. Equipment, piping, and instrument specifications
6. Process control logic diagrams
7. Layout drawings
8. Operating procedures and records
9. Maintenance procedures and records
10. Emergency response procedures
11. Safety and training manuals

Depending on the stage of the design being evaluated, some of this information may not be available.

Determining the method of assessment is the next step. The section of the process to be studied is first identified; generally, the focus is on a major piece of equipment, although a pump or a valve may be chosen depending on the hazardous nature of the materials being handled and the operating conditions of these smaller components of the system. Once the intended operation has been defined, a list of possible deviations from the intended operations is developed. The degree of deviation from normal operation is conveyed by the use of guide words, some of which are listed in Table 13.6. A relatively simple example of a HAZOP study using these guide words is shown for a boiler drum in Figure 13.3 and Table 13.7. The intent of the boiler drum operation in Figure 13.3 is to maintain the water level in the horizontal drum between 30% and 40% of its volume. As demonstrated from this example, the purpose of these guide words is to develop the thought process and encourage discussion that is related to any potential deviations in the system. When a possible deviation is recognized, the possible cause and consequences are usually determined. Alterations and appropriate action to be taken are then recommended as indicated in Table 13.7.

Final steps in the HAZOP study methodology include issuing formal reports and following up on recommendations to ensure that hazard reductions and improved process operability are the end result of the effort.

TABLE 13.6

Guide Words Used in HAZOP Studies

Guide Words	Meaning	Examples
No or Not	No part of the intention is achieved, but nothing else happens	No flow, no agitation, no reaction
More/less	Quantitative increases or decreases to the intended activity	More flow, higher pressure, lower temperature, less time
As well as	All of the intention is achieved, but some additional activity occurs	Additional component, contaminant, extra phase
Part of	Only part of the intention is achieved; part is not	Component omitted, part of multiple destinations omitted
Reverse	The opposite of the intention occurs	Reverse flow, reverse order of addition
Other than	No part of the intention is achieved. Something different happens	Wrong component, startup, shutdown, utility failure

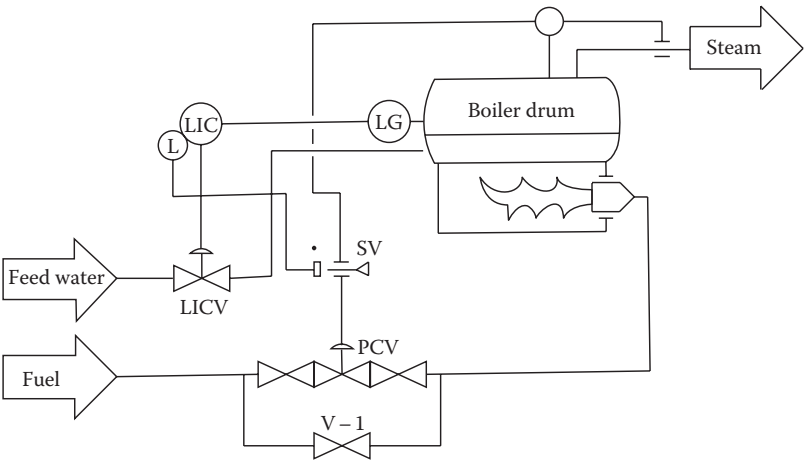


FIGURE 13.3

Example of a HAZOP study. Intention: Feed the required amount of correctly treated feed water to the boiler drum to maintain the water level in the drum between 30% and 40% full.

The overall HAZOP study method is summarized in the following steps:

1. Define objectives.
2. Define plant limits.
3. Appoint and if necessary, train a team.
4. Obtain complete preparative work.
5. Conduct examination meetings to:
 - a. Select a manageable portion of the process.
 - b. Review the flow sheet and operating procedures.

TABLE 13.7

Guide Words for HAZOP Study of Boiler Drum System in Figure 13.3

Guide Word	Deviation	Cause	Consequence
NO	NO flow of feed water	LICV (level indicator control valve) closed	Loss of level in drum and explosion of drum by flame impingement on dry shell if flame continues
	NO level in drum	Loss of feed water pressure	Same as above
		Feed water flow stops	Same as above
		Massive leak from drum	Extinguish flame
MORE	MORE than 40% level in drum	Level control fault	Excessive entrainment in stream
LESS	LESS than 30% level in drum	Similar to NO level	Loss of level in drum and explosion of drum by flame impingement on dry shell if flame continues
AS WELL AS	Contaminants AS WELL AS feed water	Water treatment fault	Fouling of boiler by corrosive steam
PART OF	PART OF feed water (treatment chemicals) omitted	Water treatment fault	Same as above
REVERSE	REVERSE flow in feed water line	Loss of feed water pressure	Steam in feed water system
OTHER THAN	Unplanned shutdown (OTHER THAN normal operation)	Utility failure	Does LICV fail closed or open?
	OTHER THAN feed water	Not possible	

- c. Agree on how the process is intended to proceed.
- d. State and record the intention of each portion of the process.
- e. Search for possible ways to deviate from the intention using the guide words.
- f. Determine possible causes for the deviation.
- g. Determine possible consequences of the deviation.
- h. Recommend action to be taken to eliminate deviation and/or mitigate consequences.
6. Issue meeting reports.
7. Follow up on recommendations.

The HAZOP study is a very useful technique (favored by the authors) that may lead to a more reliable and safer process. Whether it is applied to preliminary design stages or to the detailed layout of an existing plant, it can lead

to a better understanding of the process, possible malfunctions that could occur, and consequences of such malfunctions. HAZOP studies reduce the possibility of accidents within a process, improve their online availability, and provide a training method for the evaluation and optimization of any process, making them more reliable and cost-effective.

Illustrative Example 13.13

Briefly describe what the term “system description” refers to relative to hazard risk assessment.

Solution

“System description” is the compilation of the process/plant information needed for conducting a risk analysis. For example, to adequately understand a process and the risks it poses both on- and offsite, site locations, its surroundings, weather data, PFDs, P&IDs, layout drawings, operating and maintenance procedures, technology documentation, process chemistry, and thermophysical property data may all be required.

Illustrative Example 13.14

The word “what” appears in numerous hazard identification procedures. List some questions/comments that are related to this term.

Solution

The word “what” is used to ascertain conditions or connections that may exist for a specific piece of equipment or process in a manufacturing facility. Some of the “is” and “is not” related to conditions or connections of a system that can be related to this question of “what” are summarized as follows:

	Is	Is Not
What	What do we know?	What do we not know?
	What was observed?	What was not observed?
	What is a related problem?	What is unrelated?
	What are the constraints?	What is not a constraint?
	What is expected?	What is unexpected?
	What is the same?	What is different?
	What is the importance?	What is not important?
	What resources are needed?	
	What are the criteria?	
	What is the purpose?	

Illustrative Example 13.15

List several examples of the basic causes of ergonomic “illnesses.”

Solution

1. Incorrect posture
2. Standing too long
3. Excessive force to move something
4. Lifting too much weight
5. Lowering too much weight
6. Static loading on the body (standing/holding weight)
7. Carrying too much weight

These problems can be visualized and often anticipated during an ergonomic assessment of all jobs. The risks should be minimized through the proper application of engineering and administrative actions and controls.

Illustrative Example 13.16

It is not unusual to find reaction flasks containing volatile solvents stored in research laboratory refrigerators. Consider the following: a 500 mL flask of diethyl ether ($MW = 74.14 \text{ g/gmol}$, specific gravity = 0.713) is stored in a 15 ft^3 , unventilated refrigerator at 41°F and 1 atm. (Note: the vapor pressure of diethyl ether at 41°F is 200 mmHg).

1. How many grams of the diethyl ether must evaporate to achieve the minimum percent of ether vapors that can produce a flammable mixture? As defined earlier, this minimum percentage of vapors is the LFL, which for diethyl ether is 1.9% v/v.
2. How many grams of the ether must evaporate to reach the maximum percent of ether vapors that would still be flammable? This maximum percentage of vapor is, as was defined earlier, the UFL, which for diethyl ether is 35% v/v.
3. Comment on the hazards of such a storage practice and suggest safer alternatives.

Solution

The quantity of diethyl ether needed to reach a concentration of 1.9 vol% in the refrigerator may be found by first calculating the number of gmol of air in the refrigerator. To find the gmol air in the refrigerator, the ideal gas law, $PV = nRT$, is used with $P = 1 \text{ atm}$, $T = 41^\circ\text{F} = 5^\circ\text{C} = 278 \text{ K}$:

$$\text{Refrigerator volume} = (15.0 \text{ ft}^3)(0.0283 \text{ m}^3/\text{ft}^3) = 0.425 \text{ m}^3 = 425 \text{ L}$$

gmol air in refrigerator

$$= n = \frac{PV}{RT} = \frac{(1 \text{ atm})(425 \text{ L})}{[(0.0821 \text{ atm}\cdot\text{L/gmol}\cdot\text{K})(278 \text{ K})]} = 18.6 \text{ gmol}$$

To find the moles of diethyl ether needed to reach the 1.9% LFL, the gmol of air in the refrigerator is multiplied by 0.019 to yield

$$(18.6 \text{ gmol air}) (0.019) = 0.353 \text{ gmol diethyl ether}$$

To convert to grams of diethyl ether, the aforementioned value is multiplied by the molecular weight of diethyl ether:

$$(0.353 \text{ gmol diethyl ether}) (74.1 \text{ g/gmol}) = 26.2 \text{ g diethyl ether}$$

The LFL is reached in the refrigerator when 26.2 g, or 26.2 g/(0.713 g/mL)=36.7 mL, of diethyl ether in the flask have evaporated. Since this is being stored in a 500 mL flask and because of its high vapor pressure, adequate volumes of diethyl ether are likely available to produce a vapor concentration above its LFL.

The quantity of diethyl ether needed to reach a concentration of 36 vol% in the refrigerator (its UFL) may be found by multiplying the gmol of air in the refrigerator by 0.36 and, finally, converting gmol to g and mL of diethyl ether:

$$(18.6 \text{ gmol air}) (0.36) = 6.7 \text{ gmol diethyl ether}$$

To convert to grams of diethyl ether, the aforementioned value is multiplied by the molecular weight of diethyl ether:

$$(6.7 \text{ gmol diethyl ether}) (74.1 \text{ g/gmol}) = 496 \text{ g diethyl ether}$$

The UFL is reached in the refrigerator when 496 g, or 496 g/(0.713 g/mL)=696 mL, of diethyl ether in the flask have evaporated. Since this is being stored in a 500 mL flask, the diethyl ether vapor concentration will not reach its UFL before the flask runs dry.

As indicated earlier, it is highly likely that the evaporating diethyl ether will reach its LFL in the refrigerator. Those periods of time, such as weekends, when the refrigerator might not be opened to vent, the evaporating liquid would result in situations of greatest risk. As there is no possibility of exceeding the UFL, the hazard is not reduced by further evaporation. A storage practice such as this, which results in a significant chance of producing a flammable mixture of vapors within an enclosed space, is not advisable. An explosion proof, ventilated refrigerator should be used, the solvent should be stored in airtight containers, or the solvent should be changed/eliminated completely so that the potential fire risk in this laboratory can be eliminated.

Illustrative Example 13.17

Develop a table that lists the causes, effects, and corrective/preventive measures for the accidental release of a toxic gas from a storage tank.

TABLE 13.8

Cause and Effects Analysis for a Toxic Gas Release from Storage Tank for Illustrative Example 13.17

Cause	Major Effects	Corrective/Preventive Measures
Rupture in storage tank	Fatalities; injuries	Improve tank materials of construction
Fire in tank farm; explosion of storage tank	High release of gas into the community; fatalities	Prepare and notify community Develop fire prevention techniques and install fire control equipment in tank farm
Terrorist attack of facilities	High release of gas into the community	Prepare and notify community
Collapse of tank foundation due to hurricane, tornado, meteorite, earthquake, or auto collision	High release of gas into the community	Site downwind of community Improve structural design of foundation
Rupture in main transfer line	High release of gas into the community	Install gas analyzer with automatic diversion of flow Minimize piping
Leak in line or from tank	High release of gas into the community	Install toxic gas analyzer

Solution

The causes, effects, and corrective/preventive measures for this accidental toxic gas release are summarized in Table 13.8.

Illustrative Example 13.18

The checklist approach provides a list of sources where one might identify hazardous areas of concern in a plant. Provide at least 10 of these sources of concern related to plant hazards.

Solution

Some typical sources of hazards within a plant include:

1. Fuel storage areas
2. Pressure containers
3. Corrosives storage areas
4. Heating devices
5. Toxic chemical storage areas
6. Steam (high pressure) lines
7. Power generators
8. Flammable materials storage areas
9. Rotating equipment
10. Radiation sources
11. Transportation activities
12. Electrical transformers

Unfortunately, items NOT on the checklist can easily be overlooked, and the method is generally not suitable for use with new or relatively unproven technology.

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14

Hazard/Event Probability

14.1 Introduction

This chapter is concerned with special probability distributions and techniques used in calculations of reliability and risk. Theorems and basic concepts of probability are applied to the determination of the reliability of complex systems in terms of the reliabilities of their components. The relationship between reliability and failure rate is explored in detail. Special probability distributions for failure time are also discussed. The chapter concludes with a consideration of fault tree analysis (FTA), a special technique that figures prominently in hazard analysis and the evaluation of risk.

The causes of accidents are treated first. In the next section, equations for the reliability of series and parallel systems are established. The following section introduces several probability distribution models that are extensively used in reliability calculations in hazard risk assessment (HZRA). This is followed by a separate section on the Weibull distribution, a distribution that is used routinely in HZRA. The last section is devoted to FTA.

14.2 Accident Causes

There are a host of reasons why accidents occur in industry. The primary causes are mechanical failure, operational error (human error), process upsets, and design errors. Keep in mind that the word cause (as noted in Chapter 12) has come to mean different thing to different people. There are three steps that normally lead to an accident:

1. Initiation
2. Propagation
3. Termination

The path that an accident takes through these three steps can be determined by means of an FTA, a topic treated later in this chapter.

The chemical industry today is involved in a broad spectrum of manufacturing processes that range from biological preparations to the manufacturing of plastics and explosives. Although the basic plans and designs for these processes may be similar, each individual plant will have its own unique set of potential hazards.

Basic chemical processes that are common in industry include acylation, alkaline fusion, alkylation, amination, aromatization, calcination, carboxylation, causticization, combustion, condensation, coupling, cracking, diazotization, electrolysis, esterification, fermentation, halogenation, hydroforming, hydrolysis, isomerization, neutralization, nitration, nitrosation, oxidation, polymerization, pyrolysis, reduction, and thermal decomposition [1]. Some of these processes are considered to be more hazardous than others. Alkylation, amination, aromatization, combustion, condensation, diazotization, halogenation, nitration, oxidation, and polymerization are examples of the more hazardous processes. However, any process that exhibits one or more of the following characteristics should be considered to be extra hazardous:

1. The process is subject to explosive reaction or detonation under normal conditions.
2. The process is subject to explosive reaction or detonation when exposed to shock or abnormally high temperatures or pressures.
3. The process reacts violently with water.
4. The process is subject to spontaneous polymerization.
5. The process is subject to spontaneous heating.
6. The process is subject to exothermic reactions with the development of excessive temperatures and pressures.
7. The process normally operates at very high pressures or temperatures and may result in the massive release of flammable gases or vapors.
8. The process operates in or near the explosive range of the reactants or products.
9. The process is subject to a dust or mist explosion.
10. The process emits environmental contaminants or pollutants into the atmosphere.
11. The process uses or produces toxic substances.
12. The process uses or produces very corrosive materials.
13. The process emits dangerous radiation.
14. The process presents waste disposal problems.

Deviations from normal process conditions, as manifested by the following circumstances, must be well understood if accidents are to be prevented:

1. Abnormal temperatures
2. Abnormal pressures
3. Material flow stoppage
4. Equipment leaks or spills
5. Failure of equipment

Chemical processing under “extreme conditions” of high temperatures and pressures requires more thorough analysis and extra safeguards. As discussed in Chapter 13, explosions at higher initial temperatures and pressures are much more severe. Therefore, chemical processes under extreme conditions require specialized equipment design and fabrication. Other factors that should be considered when evaluating a chemical process are the rate and order of the reaction, stability of the reaction, and the potential human health problems caused by the raw materials used.

Under such circumstances, there is a need for high standards in equipment design, operation, and maintenance. Regardless of adequate safeguards and controls of highly technological processes, accidents do and will continue to occur. It is therefore important to examine the causes of such accidents associated with the specific pieces of equipment, supporting systems, and materials being handled. As noted earlier, the sequence of events resulting in an accident can generally be traced back to one or a combination of the following causes:

1. Equipment failure
2. Control system failure
3. Utilities and ancillary equipment outage
4. Human error
5. Fire exposure/explosions
6. Natural causes
7. Plant layout

These topics were also treated in the previous chapter.

Illustrative Example 14.1

List and briefly discuss human errors that can occur in a chemical processing plant that can lead to or cause accidents.

Solution

Some examples of human error that can occur in a chemical processing plant are:

1. *Design errors*: improper design of plant-specific processes and improper sizing and specifications for plant equipment, controls, etc.
2. *Construction errors*: problems caused by poor construction techniques or low-quality construction materials
3. *Procedural errors*: not following proper operating and/or maintenance procedures due to poor or inadequate training
4. *Management errors*: lack of attention to worker training or performance and lack of management expectations for excellence in worker and plant performance
5. *Maintenance errors*: lack of detail in maintenance requirements, scheduling, and safety procedures due to both worker and management errors

14.3 Series and Parallel Systems

Many systems consisting of several components can be classified as *series*, *parallel*, or combination systems. However, the majority of industrial facilities and process plants (units and systems) utilize many series of parallel configurations.

A *series system* is one in which the entire system fails to operate if any one of its individual components fails to operate. If such a system consists of n components that function independently, then the reliability of the system is the product of the reliabilities of the individual components. If R_s denotes the reliability of a series system and R_i denotes the reliability of its i th component, $i=1, \dots, n$, then:

$$R_s = R_1 R_2 \dots R_n = \prod_{i=1}^n R_i \quad (14.1)$$

A *parallel system* is one that fails to operate only if all of its components fail to operate. If R_i is the reliability of its i th component, then $(1 - R_i)$ is the probability that the i th component fails, where $i=1, \dots, n$. Assuming that all n components function independently, the probability that all n components fail is $(1 - R_1)(1 - R_2) \dots (1 - R_n)$. Subtracting this product from unity yields the following formula for R_p , the reliability of a parallel system:

$$R_p = 1 - (1 - R_1)(1 - R_2) \dots (1 - R_n) = 1 - \prod_{i=1}^n (1 - R_i) \quad (14.2)$$

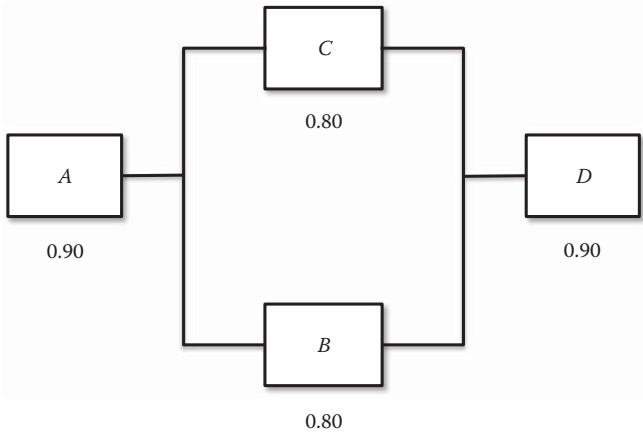


FIGURE 14.1
System with parallel and series components.

The reliability formulas for series *and* parallel systems can be used to obtain the reliability of a system that combines features of a series and a parallel system. Consider, for example, the system shown in Figure 14.1. Components *A*, *B*, *C*, and *D* have reliabilities of 0.90, 0.80, 0.80, and 0.90, respectively. The system fails to operate if *A* fails, if *B* and *C* *both* fail, or if *D* fails. Components *B* and *C* constitute a parallel subsystem connected in series to components *A* and *D*. The reliability of the parallel subsystem is obtained by applying Equation 14.2, which yields:

$$R_p = 1 - (1 - 0.80)(1 - 0.80) = 0.96$$

The reliability of the system is then obtained by applying Equation 14.1, which yields:

$$R_s = (0.90)(0.96)(0.90) = 0.78 \text{ or } 78\%$$

Illustrative Example 14.2

Determine the reliability of the electrical system shown in Figure 14.2, using the reliabilities indicated under the various components.

Solution

First identify the components connected in parallel. *A* and *B* are connected in parallel. *D* through *F* are also connected in parallel. Then compute the reliability of each subsystem of the components connected in parallel. The reliability of the parallel subsystem consisting of components *A* and *B* is

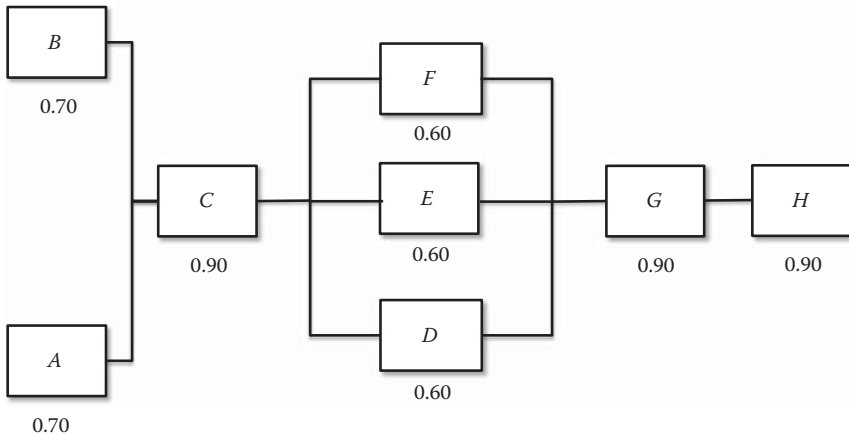
**FIGURE 14.2**

Diagram of electrical system I for Illustrative Example 14.2.

$$R_p = 1 - (1 - 0.7)(1 - 0.7) = 0.91$$

Similarly, the reliability of the parallel subsystem consisting of components *D* through *F* is:

$$R_p = 1 - (1 - 0.6)(1 - 0.6)(1 - 0.6) = 0.936$$

Multiplying the product of the reliabilities of the parallel subsystems by the product of the reliabilities of the components to which the parallel subsystems are connected in series yields:

$$R_s = (0.91)(0.9)(0.936)(0.9)(0.9) = 0.621$$

The reliability of the entire system is therefore 0.621 or 62.1%.

Illustrative Example 14.3

A failure analysis of a military overseas flight is regarded as a series system with the following components: ground crew (*A*), cockpit crew (*B*), aircraft (*C*), weather conditions (*D*), and landing accommodations (*E*). The cockpit crew is viewed as a parallel system with the following components: captain (*B*₁), copilot (*B*₂), and flight engineer (*B*₃). Landing accommodations are viewed as a parallel system with the following components: scheduled airport (*E*₁) and alternate landing sites (*E*₂ and *E*₃). Failure probabilities for the various components are estimated as follows:

$$\begin{array}{lll}
 A = 0.001 & B_3 = 0.100 & E_1 = 0.001 \\
 B_1 = 0.001 & C = 0.001 & E_2 = 0.050 \\
 B_2 = 0.010 & D = 0.0001 & E_3 = 0.100
 \end{array}$$

What is the probability of a successful flight?

Solution

First identify the components connected in parallel. B_1 , B_2 , and B_3 are connected in parallel. E_1 , E_2 , and E_3 are also connected in parallel. As with Illustrative Example 14.2, compute the reliability of each subsystem of the components connected in parallel. The reliability of the parallel subsystem consisting of components B_1 , B_2 , and B_3 is:

$$R_p = 1 - (1 - 0.999)(1 - 0.99)(1 - 0.90) = 0.999999$$

The reliability of the parallel subsystem consisting of the components E_1 , E_2 , and E_3 is:

$$R_p = 1 - (1 - 0.999)(1 - 0.95)(1 - 0.90) = 0.999995$$

Multiply the product of the reliabilities of the parallel subsystems by the product of the reliabilities of the components to which the parallel subsystems are connected in series to yield:

$$R_s = (0.999999)(0.999995)(0.999)(0.999)(0.9999) = 0.9979$$

The probability of a successful flight is therefore 0.9979 or 99.79%.

Illustrative Example 14.4

Determine the reliability of the components A , D , and G of the electrical system illustrated in Figure 14.3. Use the reliabilities indicated under the various components. The overall reliability of the system has been determined to be 0.42.

Solution

The reliability of the parallel subsystem consisting of components A and B is obtained by applying Equation 14.2, which yields:

$$R_p = 1 - (1 - 0.7)(1 - A) = 1 - (-0.3 - A + 0.7A) = 0.7 + 0.3A$$

The reliability of the parallel subsystem consisting of components D through F is:

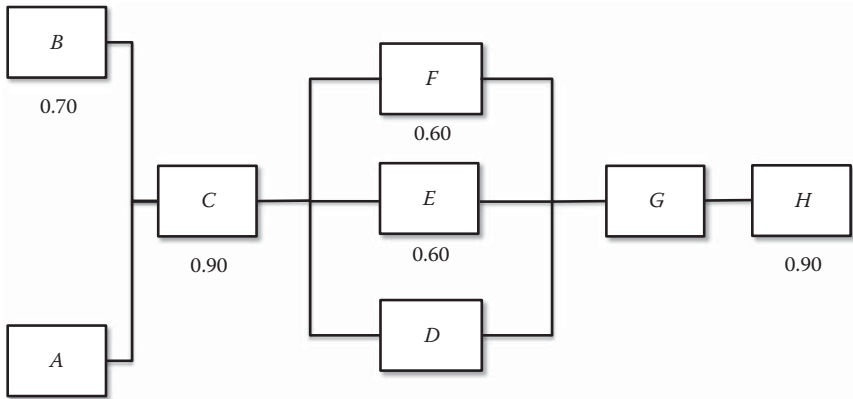
**FIGURE 14.3**

Diagram of electrical system II for Illustrative Example 14.4.

$$R_p = 1 - (1 - D)(1 - 0.6)(1 - 0.6) = (1 - 0.16)(1 - D) = 0.84 + 0.16D$$

The reliability of the entire system is obtained by applying Equation 14.1, which yields:

$$R_s = 0.42 = (0.7 + 0.3A)(0.9)(0.84 + 0.16D)(G)(0.9)$$

This single equation contains three unknowns. An infinite number of solutions are possible, including, for example,

$$A = 0; D = 0; G = 0.882$$

Illustrative Example 14.5

If a pumping system in a nuclear power plant must have a minimum reliability of 99.99%, how many pumps are required in a parallel system if each pump has a reliability of 95.1%?

Solution

Refer to Equation 14.2. The reliability for this parallel system is:

$$R_p = 1 - (1 - R_1)(1 - R_2) \dots (1 - R_n)$$

where R_i is the fractional reliability of pump i .

If the reliabilities of the pumps are assumed equal, that is, $R_1 = R_2 = \dots = R_n = R$, then:

$$R_p = 1 - (1 - R)^n$$

Noting that $R_p = 0.9999$ and $R = 0.951$, and substituting these values in the previous equation yields

$$0.9999 = 1 - (1 - 0.951)^n; 0.0001 = (1 - 0.951)^n; \ln(0.0001) = n \ln(0.049)$$

$$-9.21 = n(-3.016); n = 3.05$$

This indicates that four pumps are required to yield a reliability of at least 99.99%.

14.4 Probability Distributions

As noted in the beginning of this chapter, accidents occur because something goes wrong. That something can include a host of events/scenarios that were detailed earlier. Included in these failure events at a plant are failures of process equipment, equipment parts, ancillary equipment, etc. Fortunately, some process equipment failure rate data are available in Refs [1–4], and a particularly good source of these data is the AIChE's *Guidelines for Process Equipment Reliability Data-with Data Tables* [5]. This publication provides tables with extensive references and source of process equipment reliability. It also contains tables (with references) detailing human reliability data and information. This information provides practicing engineers and scientists with the ability to make important decisions related to HZRAs. It should be noted, however, that the "Guidelines" were prepared in 1989, and some/many of the values it contains may have changed due to equipment upgrades and technology advancements, and the reader should seek out updates to this baseline data to ensure HZRAs are as accurate and representative as possible.

Another primary source for estimates of probability and accident frequencies include historical records other than those provided in the "Guidelines." For example, specific historical data can sometimes be usefully applied as a check on frequency estimates of various subevents of a fault tree (to be discussed shortly). The use of historical data provides the most straightforward approach to the generation of accident frequency estimates but is subject to the applicability and the adequacy of the records. Care should be exercised in extracting data from long periods of the historical record over which design or operating standards or measurement criteria may have changed.

As demonstrated in Chapter 12, technical individuals need to know what the probability is of an accident occurring in their facility. Therefore, failure information and failure rate data related to the process or system of concern

is essential to conducting effective HZRAs. The “Guidelines” are, for the most part, presented as (equipment) failures per 10^6 operating hours or as failure per 10^3 demands for demand-related failure rates. These are single-valued data that do not express the varying degrees of uncertainty in the number(s) provided. In effect, the probability distribution associated with each failure or failure-rate data is not provided. Each failure value likelihood also has an associated degree of uncertainty. There are numerous qualitative ways to represent the aforementioned likelihood using words like “probably,” “perhaps,” or even “maybe.” The statement that an accident is “highly unlikely” could mean different things to different people.

Because these terms are vague, a more precise way to represent the uncertainty is highly desirable. One way to express the likelihood quantitatively is to use a numerical value, termed the probability, to express its likelihood of occurring. The statement that there is a 2% chance of the accident occurring is obviously more precise and less vague than saying the chance of an accident is very low. The probability can be expressed as a fractional number, for example, 0.37, or a percent number from 0% to 100%, for example, 37%. Naturally, the sum of fractional probabilities for all possible states of occurrence must be 1.0.

The probability variation noted earlier is another factor that needs to be considered in an HZRA. This includes not only the variations of the reported single-valued data but also probability variations with time, e.g., the annual probability of an earthquake occurring of a given magnitude or the probability variation with time of a NASA spacecraft failing immediately after liftoff. The need for this probability information is again noted with reference to Figure 12.1. It is for this reason that this chapter treats the general subject of probability, particularly as it applies to hazards and events.

Before proceeding to probability distributions, it behooves the reader to grasp the concept of the probability distribution function. In mathematics, a *function* is defined as a relationship between a quantity that depends on another quantity or quantities. *Probability distributions* are an integral part of the general subject of statistics. There are three distributions of concern that arise in risk assessment studies.

1. *Probability distribution function (pdf)*. A pdf is a distribution of probabilities of the values of a dependent variable as a function of a value of an independent variable (usually time). In the context of HZRA, the pdf represents the probability that a given event or accident will occur *at or before* a specified time.
2. *Probability density function*. The probability density function describes the relative values of the probability (or likelihood of the occurrence) of *all* possible values of the independent variable.
3. *Cumulative distribution function (cdf)*. A cdf is the cumulative sum of all probabilities of a dependent variable *less than or equal* to a specific

value of an independent variable (usually time). In HZRA, a cdf provides information on ascending (or increasing) values of the accident probabilities at increasing values of operating time or time since a previous component or system failure.

This chapter is devoted to providing general properties of various pdfs for discrete and continuous random variables, as well as an introduction to the cdf. Special pdfs finding extensive application in HZRA are considered later in this section. Although the mathematical development to follow will focus on *continuous* rather than *discrete* random variables, the material can be easily extended to include the latter topic.

The pdf of a continuous random variable X has the following properties:

$$\int_a^b f(x) dx = P(a < X < b) \quad (14.3)$$

$$f(x) \geq 0 \quad (14.4)$$

$$\int_{-\infty}^{\infty} f(x) dx = 1 \quad (14.5)$$

Equation 14.3 indicates that the pdf of a continuous random variable generates probability by integration of the pdf for the interval over which the probability is required. When this interval contracts to a single value, the integral over the interval becomes zero. Therefore, the probability associated with any particular value of a continuous random variable is zero. Consequently, if X is continuous,

$$P(a \leq X \leq b) = P(a < X \leq b) = P(a < X < b) = P(a \leq X < b) \quad (14.6)$$

Equation 14.4 restricts the values of $f(x)$ to nonnegative numbers. Equation 14.5 follows from the fact that:

$$P(-\infty < X < \infty) = 1 \quad (14.7)$$

As an example of the pdf of a continuous random variable, consider the pdf of the time X in hours between successive failures of an aircraft air-conditioning system. Suppose the pdf of X is specified by:

$$f(x) = 0.01 e^{-0.01x}, \quad x > 0; \quad f(x) = 0; \quad \text{elsewhere} \quad (14.8)$$

The expression $P(a < X < b)$ can be interpreted geometrically as the area under the pdf curve over the interval (a, b) . Integration of the pdf over the interval yields the probability assigned to the interval. For example, the probability that the time in hours between successive failures of the aforementioned aircraft air-conditioning system is greater than 6 but less than 10 is:

$$\begin{aligned}
 P(6 < X < 10) &= \int_6^{10} 0.01e^{-0.01x} dx = 0.01 \int_6^{10} e^{-0.01x} dx = 0.01 \left[-\left(\frac{1}{0.01}\right) e^{-0.01x} \right]_6^{10} \\
 P(6 < X < 10) &= -e^{-0.01x} \Big|_6^{10} = -e^{-(0.01)10} - (-e^{-(0.01)6}) = -e^{-0.1} + e^{-0.06} \\
 &= -0.9048 + 0.9418 = 0.037
 \end{aligned}$$

The pdf of a continuous random variable (Equation 14.3) is a function that, when integrated over an interval, gives the probability that the random variable values assume in that interval.

Alternately, the pdf of a discrete random variable is a function that assigns probability to each of the possible values of the discrete random variable. If $f(x)$ is the pdf of a discrete random variable X , then $f(x) = P(X = x)$ is the probability assigned to the value x of the random variable X .

Another function used to describe the probability distribution of a random variable X is the aforementioned cdf. If $f(x)$ specifies the pdf of a random variable X , then $F(x)$ is used to specify the cdf. For both discrete and continuous random variables, the cdf of X is defined by

$$F(x) = P(X \leq x); \quad -\infty < x < \infty \quad (14.9)$$

Note that the cdf is defined for all real numbers, not just the values assumed by the random variable. $F(x)$ is the cumulative sum of all probabilities assigned to real numbers less than or equal to x . Shaefer and Theodore provide additional details [3].

Several probability distributions are presented below that figure prominently in reliability calculations and HZRAs. Their pdfs, principal characteristics, and their application to HZRA are highlighted.

14.4.1 Binomial Distribution

Consider n independent performances of a random experiment with mutually exclusive outcomes that can be classified as a “success” or “failure.” The words “success” and “failure” are to be regarded as labels for two mutually exclusive categories of outcomes of the random experiment rather than the ordinary connotations of success or failure in this analysis. Assume that p ,

the probability of success of any performances of the random experiment, is constant. Let q be the probability of failure, so that

$$q = 1 - p \quad (14.10)$$

The probability distribution of X , the number of successes in n performances of the random experiment, is the binomial distribution, with a pdf specified by:

$$f(x) = \frac{n!}{x!(n-x)!} p^x q^{n-x}; \quad x = 0, 1, \dots, n \quad (14.11)$$

where $f(x)$ is the probability of x successes in n performances. One can show that the expected value of the random variable X is np and its variance is npq [3].

As a simple example of the binomial distribution, consider the probability distribution of the number of defective items in a sample of five items drawn with replacement from a lot of 1000 items, 50 of which are defective. If “success” is associated with drawing a defective item from the lot, then the result of each drawing can be classified success (defective item) or failure (nondefective item) using a binomial distribution. Since the sample of items is drawn with replacement (i.e., each item in the sample is returned before the next is drawn from the lot), the probability of success remains constant at 0.05. Substituting into Equation 14.11 the values $n=5$, $p=0.05$, and $q=0.95$ yields:

$$f(x) = \frac{5!}{x!(5-x)!} (0.05)^x (0.95)^{5-x}; \quad x = 0, 1, 2, 3, 4, 5$$

as the pdf for X , the number of defective items in the sample. The probability that the sample contains exactly three defective items is given by:

$$P(X = 3) = \frac{5!}{3!2!} (0.05)^3 (0.95)^2 = 0.0011$$

The binomial distribution can be used to calculate the reliability of a *redundant system* [6], with a redundant system being one consisting of n identical components that fails only if more than r components fail. Familiar examples include single-usage equipment such as missile engines, short-life batteries, and flash bulbs, which are required to operate for one time period and are not reused. If “success” is associated with the failure of a component, that the n components are independent with respect to failure, and that the reliability of each component is $1-p$, then X , the number of failures, has the

binomial pdf of Equation 14.11, and the reliability of the redundant system failing from r number of component failures is:

$$P(X \leq r) = \sum_{x=0}^r \frac{n!}{x!(n-x)!} p^x q^{n-x} \quad (14.12)$$

For example, consider the case of a standby redundancy system consisting of one operating pump and two on standby so that the system can survive two failures. Assume that the pumps are independent with respect to failure and that each has a probability of failure of 0.1. Thus, $n=3$, $r=2$, and $1-p=0.9$. The reliability of the system is found from Equation 14.12 to be:

$$P(X \leq 2) = \sum_{x=0}^2 \frac{3!}{x!(3-x)!} (0.10)^x (0.90)^{3-x} = 0.999$$

14.4.2 Poisson Distribution

The pdf of the Poisson distribution can be derived by taking the limit of the binomial pdf as $n \rightarrow \infty$, $p \rightarrow 0$, and $np = \mu$ remain constant. The Poisson pdf is given by:

$$f(x) = \frac{e^{-\mu} \mu^x}{x!}; \quad x = 0, 1, 2, \dots \quad (14.13)$$

Here, $f(x)$ is the probability of x occurrences of an event with an average rate of single event occurrence of μ times per unit of space or time. Both the mean and the variance of the random variable X having a Poisson distribution are μ .

The Poisson pdf can be used to approximate probabilities obtained from the binomial pdf given in Equation 14.11 when n is large and p is small. In general, good approximations will result when n exceeds 10 and p is less than 0.05. When n exceeds 100 and np is less than 10, the approximation will generally be excellent.

If λ is the failure rate of each component of a system, then λt is the average number of failures per unit of time, t . The probability of x failures in the specified unit of time is obtained by substituting $\mu = \lambda t$ in Equation 14.13 to obtain:

$$f(x) = \frac{e^{-\lambda t} (\lambda t)^x}{x!}; \quad x = 0, 1, 2, \dots \quad (14.14)$$

Suppose, for example, that the average number of airplane crashes per year in a certain country is 2.5. What is the probability of four or more crashes

during the next year? Substituting $\lambda = 2.5/\text{year}$ and $t = 1$ year in Equation 14.14 yields:

$$f(x) = \frac{e^{-2.5}(2.5)^x}{x!}; \quad x = 0, 1, 2, \dots$$

as the pdf of X , the number of airplane crashes in one year. The probability of four or more airplane crashes next year is then

$$P(X \geq 4) = 1 - P(X \leq 3) = 1 - \sum_{x=0}^3 \frac{e^{-2.5}(2.5)^x}{x!} = 1 - 0.76 = 0.24 = 24\%$$

As another example, suppose that the number of breakdowns of personal computers during 1000h of operation of a computer center is 3. What is the probability of no breakdowns during a 10h work period? Substituting $\lambda = 3/1000 = 0.003/\text{h}$ and $t = 10\text{h}$ into Equation 14.14 yields:

$$f(x) = \frac{e^{-(0.003 \times 10)}(0.003 \times 10)^x}{x!} = \frac{e^{-(0.03)}(0.03)^x}{x!}; \quad x = 0, 1, 2, \dots$$

as the pdf of X , the number of breakdowns in a 10h period. The probability of no breakdowns in a 10h work period is then:

$$P(X = 0) = e^{-0.03} = 0.97$$

In addition to the applications cited earlier, the Poisson distribution can be used to obtain the reliability of a standby redundancy system [5], in which one unit is in the operating mode and n identical units are in standby mode. Unlike a parallel system where all units in the system are active, in the standby redundancy system, the standby units are inactive. If all units have the same failure rate in the operating mode, unit failures are independent, standby units have zero failure rate in the standby mode, and there is perfect switchover to a standby unit when the operating unit fails, then the reliability R of the standby redundancy system is given by:

$$R = \sum_{x=0}^n \frac{e^{-\lambda t}(\lambda t)^x}{x!} \quad (14.15)$$

This is the probability if n or fewer unit failures in the time period specified by t . For example, consider the case of a standby redundancy system with one operating unit and one on standby (i.e., a system that can survive one

failure). If the failure rate is 2 units per year, then the 6 month reliability of the system is obtained by substituting $n=1$, $\lambda=2/\text{year}$, and $t=0.5$ year into Equation 14.15, which gives:

$$R = \sum_{x=0}^1 \frac{e^{-1}(1)^x}{x!} = 0.74 = 74\%$$

as the 6 month reliability of the system. Providing a second standby unit so that the system can survive two failures, the operating unit and one standby unit, increases the 6 month reliability of the system to ($n=2$, $\lambda=2/\text{year}$, and $t=0.5$ year):

$$R = \sum_{x=0}^2 \frac{e^{-1}(1)^x}{x!} = 0.92 = 92\%$$

14.4.3 Exponential Distribution

The exponential distribution is an important distribution in that it represents the distribution of the time required for a single event from a Poisson process to occur. In particular, in sampling from a Poisson distribution with parameter μ , the probability that no event occurs during time $=0$ to t is $e^{-\lambda t}$. Consequently, the probability that an event will occur during time $=0$ to t is:

$$f(t) = 1 - e^{-\lambda t} \quad (14.16)$$

This represents the cdf of t . One can therefore show that the pdf is [3]:

$$f(t) = e^{-\lambda t} \quad (14.17)$$

Note that the parameter $1/\lambda$ (sometimes denoted as μ) is the expected value. Normally, the reciprocal of this value is specified and represents the expected value of $f(t)$.

Because the exponential function appears in the expression for both the pdf and cdf, the distribution is justifiably called the *exponential distribution*. A typical plot of the pdf of x for an exponential distribution is provided in Figure 14.4.

The cumulative exponential distribution function can be obtained from the pdf (with x replacing t) as:

$$F(x) = \int_0^x \lambda e^{-\lambda x} dx = 1 - e^{-\lambda x} \quad (14.18)$$

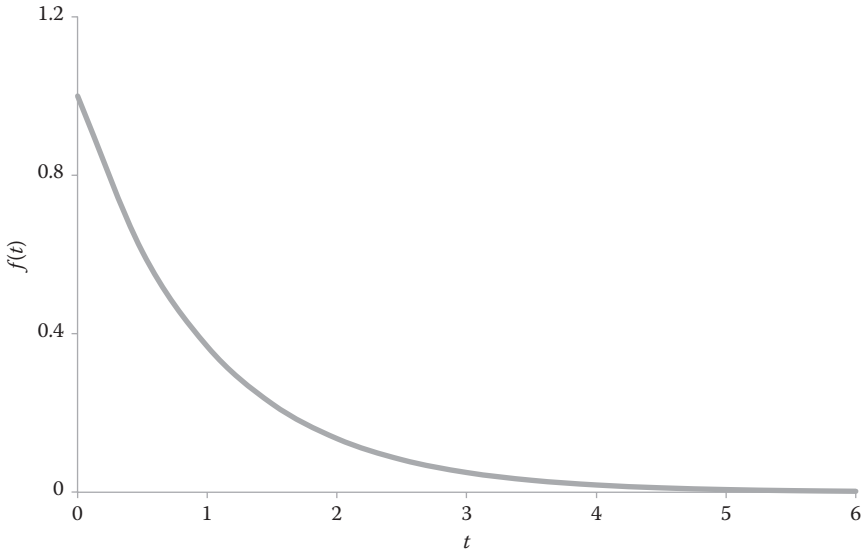


FIGURE 14.4
Exponential distribution.

All that is required to solve the cdf is a simple evaluation of the negative exponent in Equation 14.18.

In statistical and reliability applications, one often encounters a random variable's conditional failure density or hazard function, $g(x)$. In particular, $g(x)dx$ is the probability that a “product” will fail during the time period x to $x + dx$ under the condition that it had not failed before time x . Consequently,

$$g(x) = \frac{f(x)}{1 - F(x)} \quad (14.19)$$

If the probability density function $f(x)$ is exponential, with parameter λ , it follows from Equations 14.17 and 14.18 that:

$$g(x) = \frac{\lambda e^{-\lambda x}}{1 - (1 - e^{-\lambda x})} = \frac{\lambda e^{-\lambda x}}{e^{-\lambda x}} = \lambda \quad (14.20)$$

Equation 14.20 indicates that the failure probability for an exponential distribution is constant, irrespective of time. It implies that the probability that a component, whose time-to-failure distribution is exponential, fails in an instant during the first hour of its life is the same as its failure probability during an instant in the thousandth hour—presuming it has survived up to that instant in time. It is for this reason that the parameter λ is usually

referred to in operational life test applications as the *failure rate*. This definition generally has meaning only with an exponential distribution.

This natural association with operational life testing, as well as the fact that it is very tractable mathematically makes the exponential distribution attractive as representing the distribution of the operating life of a complex system or a series of complex systems. In fact, the exponential distribution is as prominent in reliability analysis as the normal distribution is in other branches of statistics and engineering.

It has been shown theoretically that this distribution provides a reasonable model for systems designed with a limited degree of redundancy that are made up of many components, none of which has a high probability of failure. This is especially true when low component failure rates are maintained by periodic inspection and replacement, or in situations in which failure is a function of outside phenomena rather than a function of previous conditions of components within the system. On the other hand, the exponential distribution often cannot represent individual component life and it is sometimes questionable even as a system model.

14.4.4 Normal Distribution

When T , time to failure, has a normal distribution, its pdf is given by:

$$f(t) = \frac{1}{\sqrt{2\pi}\sigma} \exp \left[-\frac{1}{2} \left(\frac{t-\mu}{\sigma} \right)^2 \right]; \quad -\infty < t < \infty \quad (14.21)$$

where

μ is the mean value of T

σ is its standard deviation

The graph of $f(t)$ is the familiar bell-shaped curve shown in Figure 14.5. The reliability function corresponding to normally distributed failure time can be shown as follows [7]:

$$R(t) = P(T > t) = \frac{1}{\sqrt{2\pi}\sigma} \int_t^{\infty} \exp \left[-\frac{1}{2} \left(\frac{t-\mu}{\sigma} \right)^2 \right] dt \quad (14.22)$$

If T is normally distributed with mean μ and standard deviation σ , then the random variable $(T-\mu)/\sigma$ is normally distributed with mean 0 and standard deviation 1. The term $(T-\mu)/\sigma$ is called a "standard normal variable," and the graph of its pdf is called a "standard normal curve." Table 14.1 is a tabulation of areas under a standard normal curve to the right of nonnegative values of z_0 [3,7]. Probabilities about a standard normal variable Z can be determined from the table. For example,

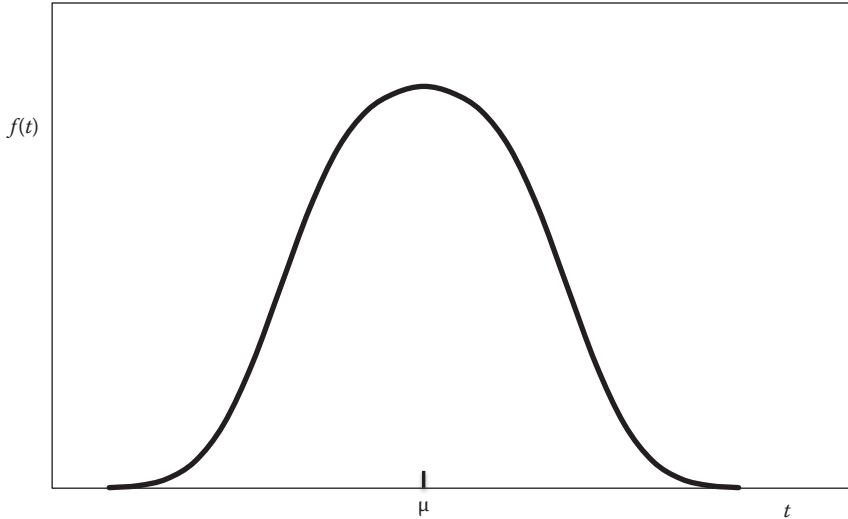


FIGURE 14.5
Normal pdf of time to failure.

$$P(Z > 1.54) = 0.062$$

is obtained directly from the table as the area to the right of $Z = 1.54$. The symmetry of the standard normal curve about zero implies that the area to the right of zero is 0.5 and the area to the left of zero is 0.5. Consequently,

$$P(0 < Z < 1.54) = 0.5 - 0.062 = 0.438$$

Also, because of symmetry:

$$P(-1.54 < Z < 0) = 0.438 \text{ and } P(Z < -1.54) = 0.062$$

Note that the area to the right of 1.54 is 0.062. The following probabilities can also be deduced from Figure 14.6 and Table 14.1.

$$P(-1.54 < Z < 1.54) = 0.876$$

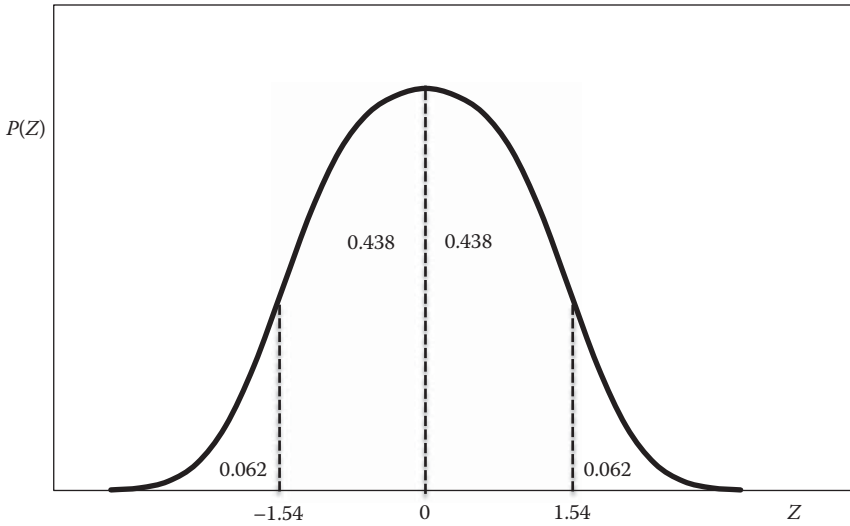
$$P(Z < 1.54) = 0.938; P(Z > -1.54) = 0.938$$

Table 14.1 also can be used to determine probabilities concerning normal random variables that are not standard normal variables. The required

TABLE 14.1
Standard Normal, Cumulative Probability in Right-Hand Tail (for Negative Values of Z, Areas Are Found by Symmetry)

Z ₀	Next Decimal Place of Z ₀									
	0	1	2	3	4	5	6	7	8	9
0.0	.500	.496	.492	.488	.484	.480	.476	.472	.468	.464
0.1	.460	.456	.452	.448	.444	.440	.436	.433	.429	.425
0.2	.421	.417	.413	.409	.405	.401	.397	.394	.390	.386
0.3	.382	.378	.374	.371	.367	.363	.359	.356	.352	.348
0.4	.345	.341	.337	.334	.330	.326	.323	.319	.316	.312
0.5	.309	.305	.302	.298	.295	.291	.288	.284	.281	.278
0.6	.274	.271	.268	.264	.261	.258	.255	.251	.248	.245
0.7	.242	.239	.236	.233	.230	.227	.224	.221	.218	.215
0.8	.212	.209	.206	.203	.200	.198	.195	.192	.189	.187
0.9	.184	.181	.179	.176	.174	.171	.189	.166	.164	.161
1.0	.159	.156	.154	.152	.149	.147	.145	.142	.140	.138
1.1	.136	.133	.131	.129	.127	.125	.123	.121	.119	.117
1.2	.115	.113	.111	.109	.107	.106	.104	.102	.100	.099
1.3	.097	.095	.093	.092	.090	.089	.087	.085	.084	.082
1.4	.081	.079	.078	.076	.075	.074	.072	.071	.069	.068
1.5	.067	.066	.064	.063	.062	.061	.059	.058	.057	.056
1.6	.055	.054	.053	.052	.051	.049	.048	.047	.046	.046
1.7	.045	.044	.043	.042	.041	.040	.039	.038	.038	.037
1.8	.036	.035	.034	.034	.033	.032	.031	.031	.030	.029
1.9	.029	.028	.027	.027	.026	.026	.025	.024	.024	.023
2.0	.023	.022	.022	.021	.021	.020	.020	.019	.019	.018
2.1	.018	.017	.017	.017	.016	.016	.015	.015	.015	.014
2.2	.014	.014	.013	.013	.013	.012	.012	.012	.011	.011
2.3	.011	.010	.010	.010	.010	.009	.009	.009	.009	.008
2.4	.008	.008	.008	.008	.007	.007	.007	.007	.007	.006
2.5	.006	.006	.006	.006	.006	.005	.005	.005	.005	.005
2.6	.005	.005	.004	.004	.004	.004	.004	.004	.004	.004
2.7	.003	.003	.003	.003	.003	.003	.003	.003	.003	.003
2.8	.003	.002	.002	.002	.002	.002	.002	.002	.002	.002
2.9	.002	.002	.002	.002	.002	.002	.002	.001	.001	.001
Z ₀	Detail of Tail (e.g., .2135 Means 0.00135)									
2.	. ₁ 228	. ₁ 179	. ₁ 139	. ₁ 107	. ₂ 820	. ₂ 621	. ₂ 466	. ₂ 347	. ₂ 256	. ₂ 187
3.	. ₂ 135	. ₃ 968	. ₃ 687	. ₃ 483	. ₃ 337	. ₃ 233	. ₃ 159	. ₃ 108	. ₄ 723	. ₄ 481
4.	. ₄ 317	. ₄ 207	. ₄ 133	. ₅ 854	. ₅ 541	. ₅ 340	. ₅ 211	. ₅ 130	. ₆ 793	. ₆ 479
5.	. ₆ 287	. ₆ 170	. ₇ 996	. ₇ 579	. ₇ 333	. ₇ 190	. ₇ 107	. ₈ 599	. ₈ 332	. ₈ 182
	0	1	2	3	4	5	6	7	8	9

Source: Shaefer, S. and L. Theodore, *Probability and Statistics Applications for Environmental Science*, CRC Press, Boca Raton, FL, 2007.

**FIGURE 14.6**

Areas under a standard normal curve.

probability is first converted to an equivalent probability about a standard normal variable. For example, if T , the time to failure, is normally distributed with mean $\mu = 100$ and standard deviation $\sigma = 2$, then $(T - 100)/2$ is a standard normal variable and:

$$P(98 < T < 104) = P\left[-1 < \frac{T - 100}{2} < 2\right] = P(-1 < Z < 2)$$

$$P(98 < T < 104) = 0.341 + 0.477 = 0.818$$

For any random variable X that is normally distributed with mean μ and standard deviation σ ,

$$P(\mu - \sigma < X < \mu + \sigma) = P\left(-1 < \frac{X - \mu}{\sigma} < 1\right) = P(-1 < Z < 1) = 0.68 \quad (14.23)$$

$$P(\mu - 2\sigma < X < \mu + 2\sigma) = P\left(-2 < \frac{X - \mu}{\sigma} < 2\right) = P(-2 < Z < 2) = 0.95 \quad (14.24)$$

$$P(\mu - 3\sigma < X < \mu + 3\sigma) = P\left(-3 < \frac{X - \mu}{\sigma} < 3\right) = P(-3 < Z < 3) = 0.997 \quad (14.25)$$

The probabilities given in Equations 14.23 through 14.25 can be used to interpret the standard deviation of a sample of observations of a normal random variable as a measure of dispersion about the sample mean \bar{X} .

14.4.5 Log-Normal Distribution

A nonnegative random variable X has a log-normal distribution whenever $\ln(X)$, the natural logarithm of X , has a normal distribution. The pdf of a random variable X having a log-normal distribution is specified by:

$$f(x) = \frac{1}{\sqrt{2\pi}\beta} x^{-1} \exp\left[-\frac{(\ln x - \alpha)^2}{2\beta^2}\right], \quad x > 0; \quad f(x) = 0, \text{ elsewhere} \quad (14.26)$$

The mean and variance of a random variable X having a log-normal distribution are given by Equations 14.27 and 14.28, respectively, as:

$$\mu = e^{(\alpha + \beta^2)/2} \quad (14.27)$$

$$\sigma^2 = e^{2\alpha + \beta^2} (e^{\beta^2} - 1) \quad (14.28)$$

Probabilities concerning random variables having a log-normal distribution can be calculated using tables of the normal distribution. If X has a log-normal distribution with parameters α and β , then $\ln(X)$ has a normal distribution with $\mu = \alpha$ and $\sigma = \beta$. Probabilities of X can therefore be converted into equivalent probabilities of $\ln(X)$. Suppose, for example, that X has a log-normal distribution with $\alpha = 2$ and $\beta = 0.1$. Then:

$$P(6 < X < 8) = P(\ln(6) < \ln(X) < \ln(8))$$

$$P(6 < X < 8) = P\left[\frac{\ln(6) - 2}{0.1} < \frac{\ln(X) - 2}{0.1} < \frac{\ln(8) - 2}{0.1}\right]$$

$$P(6 < X < 8) = P(-2.08 < Z < 0.79) = 0.78$$

Estimates of the parameters α and β in the pdf of a random variable X having a log-normal distribution can be obtained from a sample of observations on X by making use of the fact that $\ln(X)$ is normally distributed with mean α and standard deviation β . Therefore, the mean and standard deviation of the natural logarithms of the sample observations on X furnish estimates of α and β . To illustrate the procedure, suppose the time to failure T , in thousands of hours, was observed for a sample of five electric motors. The observed values of T were 8, 11, 16, 22, and 34, and the natural log values of these observations are 2.08, 2.40, 2.77, 3.09, and 3.53, respectively. Assuming that T has a

log-normal distribution, the estimates of the parameters α and β in the pdf are obtained from the mean and standard deviation of the natural logs of the observations on T , or for this example, $\alpha=2.77$ and $\beta=0.57$.

A modified form of a log-normal distribution is the so-called "Probit" function (some refer to it as a log-normal model). In its basic form, the probit model (e.g., as applied to individuals exposed to a toxic chemical) is expressed as:

$$P = a_0 + a_1 \log(c^{a_2} t) \quad (14.29)$$

where

P is percent, fraction, or number of individuals affected

a_0, a_1, a_2 are constants

c is chemical concentration, consistent units

t is time

Although the model is employed at times to represent toxicological data, it finds its main application in emergency/accidental chemical exposures.

In addition to the probability distributions discussed earlier, there are several other well-known distributions that can be used in HZRA calculations. A brief summary of these distributions is provided in Table 14.2. A short description of each of these discrete variable distributions not covered earlier is provided in Table 14.3.

Illustrative Example 14.6

The probability that an accidental exposure to a toxic chemical will be fatal is 0.80. Find the probability of the following events for a group of 15 workers if a binomial distribution can be used to express the probability of fatalities from this exposure.

1. At least nine will die.
2. From four to eight will die.

TABLE 14.2

Probability Distributions

Statistical Class	Distribution
Discrete	Geometric
	Multinomial
Continuous	Extreme value
	Gamma
	Rayleigh
	Rectangular
	Weibull

TABLE 14.3
Statistical Distribution Details for Discrete Random Variables

Probability Distribution	Description	Application
Geometric	Probability distribution of the number of failures before the first success occurs. It is the discrete analog of the exponential distribution, where parameter p is analogous to λ_c . Distribution assumes “memory less” property of independent trials	Can be applied to discrete failure on demand data in absence of other information
Multinomial	Probability distribution of the number of failures in n independent demands in which, at each trial, there are more than two possible outcomes	Appropriate for situations similar to those for binomial distribution, except more than two outcomes can be found

Solution

For Event 1, apply a binomial distribution,

$$P(\text{at least 9 will die}) = P(X \geq 9); \quad p = 0.8, q = 0.2$$
$$P(\text{at least 9 will die}) = \sum_{x=9}^{15} \frac{15!}{x!(15-x)!} (0.8)^x (0.2)^{15-x}$$
$$P(\text{at least 9 will die}) = 0.0430 + 0.1032 + 0.1876 + 0.2501 + 0.2309$$
$$+ 0.1319 + 0.0352 = 0.982 = 98.2\% \tag{14.30}$$

This calculation can be performed by longhand or obtained directly from binomial tables [6].
For Event 2,

$$P(4 \leq X \leq 8) = 1.0 - P(X \geq 9) - P(0 \leq X \leq 4)$$

One notes almost immediately that because of the last term on the right-hand side of Equation 14.30,

$$P(0 \leq X \leq 4) \approx 0$$

Therefore,

$$P(4 \leq X \leq 8) = 1.0 - 0.982 - 0.0 = 0.018 = 1.8\%$$

Illustrative Example 14.7

A safety shower contains (for emergency rinsing purposes) 20 independent sprays, each of which fails with a probability of 0.10. The system fails only if four or more of the sprays fail. What is the probability that the unit will fail?

Solution

Let X denote the number of sprays that fail. The term X has a binomial distribution with $n=20$ and $p=0.10$. The probability that the system fails is given by:

$$P(X \geq 4) = \sum_{x=4}^{20} \frac{20!}{x!(20-x)!} (0.1)^x (0.9)^{20-x} = 1 - \sum_{x=0}^3 \frac{20!}{x!(20-x)!} (0.1)^x (0.9)^{20-x}$$

$$\begin{aligned} P(X \geq 4) &= 1 - (0.1216 + 0.2702 + 0.2852 + 0.1901) = 1 - 0.8671 \\ &= 0.1329 = 13.3\% \end{aligned}$$

Illustrative Example 14.8

The average number of defective welds detected at the final examination of the tail section of an aircraft is five. What is the probability of detecting at least one defective weld during the final examination of the tail section?

Solution

Since this problem is asking for an assessment of the probability of defects over an area of tail section, the Poisson distribution is appropriate for this solution. The given average is the average number of defective welds detected at the final inspection of an aircraft tail section. The unit of space connected with the given average is the space occupied by the tail section of the aircraft. Therefore, the associated unit of space is the same as the space occupied by the tail section of the aircraft. Because both the unit of space connected with the given average and the unit of space connected with the required area are the same, their quotient is one.

The probability required is the probability of detecting at least one defective weld at the final inspection of the tail section. The given average number of defective welds is five. Multiplication by 1 yields the value of μ as five. Substituting this value of μ into the Poisson pdf yields:

$$f(x) = \frac{e^{-5}(5)^x}{x!}; \quad x = 0, 1, 2, \dots$$

Substituting for x the number of occurrences whose probability is required, i.e., 0 weld defects in this case, the probability of detecting at least one defective weld is:

$$P(X \geq 0) = 1 - P(X = 0) = 1 - \frac{e^{-5}(5)^0}{0!} = 0.9933 = 99.33\%$$

The reader should note that the Poisson pdf provides the probability of x occurrences over the unit of space associated with the required probability. As indicated earlier, one must substitute for x in the pdf the number of occurrences whose probability is required. However, more than one value of x may have to be substituted if the required probability is the sum of the probabilities for several values of x .

Illustrative Example 14.9

Over the last 10 years, a local hospital reported that the number of deaths per year due to temperature inversions (air pollution) was 0.5. What is the probability of exactly three deaths in a given year? What is the annual probability of three or more deaths being attributed to temperature inversions?

Solution

This problem relates to the average number of fatalities over a year and can be solved using the Poisson distribution. First, the annual probability of exactly three fatalities is calculated by substituting values given earlier into Equation 14.13 with $X=3$:

$$P(X = 3) = \frac{e^{-0.5}(0.5)^3}{3!} = 0.0126 = 1.26\%$$

For the case of three or more fatalities, the following substitutions can be made:

$$\begin{aligned} P(X \geq 3) &= 1 - P(X \leq 2) = 1 - \sum_{x=0}^2 \frac{e^{-0.5}(0.5)^x}{x!} = 1 - 0.60065 - 0.3033 \\ &\quad - 0.0758 = 0.0227 = 2.27\% \end{aligned}$$

Illustrative Example 14.10

Assume the number of particles emitted by a radioactive substance has a Poisson distribution with an average emission of one particle per second.

1. Find the probability that at most one particle will be emitted in 3 s.
2. How low of an emission rate would be required to yield a probability of the emission of at most one particle in 3 s greater than 0.80?

Solution

For Part (1), let X denote the number of radioactive particles emitted in 3 s. Because $\lambda=1$ and $t=3$, $\mu=3$. Therefore, the pdf of X assuming a Poisson distribution is:

$$f(x) = \frac{e^{-3}(3)^x}{x!}; \quad x = 0, 1, 2, \dots$$

The probability that at most one particle will be emitted in 3 s is:

$$P(X \leq 1) = \sum_{x=0}^1 \frac{e^{-3}(3)^x}{x!} = e^{-3} + e^{-3}(3) = 0.0498 + 0.1494 = 0.1992 = 19.92\%$$

For Part (2), let λ be the required emission rate per second, then $\mu=3\lambda$. Then the pdf of X is:

$$f(x) = \frac{e^{-3\lambda}(3\lambda)^x}{x!}$$

In addition, for an emission of a maximum of one particle in 3 s, the probability is:

$$\begin{aligned} P(X \leq 1) &= \sum_{x=0}^1 \frac{e^{-3\lambda}(3\lambda)^x}{x!} = P(X=0) + P(X=1) = e^{-3\lambda} \\ &+ 3\lambda(e^{-3\lambda}) = e^{-3\lambda}(1 + 3\lambda) \end{aligned}$$

For the probability of emission of at most one particle in 3 s to be at least 0.80, λ , the emission rate per second, must be such that:

$$P(X \leq 1) = e^{-3\lambda}(1 + 3\lambda) \leq 0.80$$

This can be solved using trial-and-error or the goal seek function in Excel or on a graphic calculator. For $\lambda=0.3$,

$$e^{-3\lambda}(1 + 3\lambda) - 0.80 = +0.0275$$

For $\lambda=0.2$,

$$e^{-3\lambda}(1 + 3\lambda) - 0.80 = -0.0781$$

Using the goal seek function in Excel, $\lambda=0.2748$ is obtained. Therefore, an emission rate of 0.275 particles/s or less is required to yield a probability of the emission of at most one particle in 3 s of ≥ 0.80 .

**FIGURE 14.7**

Exponential failure rate: series system for Illustrative Example 14.11.

Illustrative Example 14.11

Consider the system shown in Figure 14.7. Determine the reliability, R , if the operating time for each unit is 5000 h. Each component has an exponential failure rate that results in their reliability being described as $R_i = e^{-\lambda_i t}$ for $t = \text{time in hours}$. The failure rates of components A and B , λ , are 3×10^{-6} and 4×10^{-6} failures/h, respectively. The term λ may be viewed as the reciprocal of the average time to failure.

Solution

Because this is a series system, the following expression can be used for the reliability of the system as a whole:

$$R_S = R_A R_B \quad (14.31)$$

Using an exponential failure rate expression for each component yields:

$$R_A = e^{-3 \times 10^{-6}(5000)} = e^{-0.015} = 0.9851$$

and

$$R_B = e^{-4 \times 10^{-6}(5000)} = e^{-0.02} = 0.9802$$

Therefore,

$$R_S = (0.9851)(0.9802) = 0.9656 = 96.6\%$$

Illustrative Example 14.12

Estimate the probability that a pump will survive at least three times its expected life. Assume the exponential distribution applies to its failure rate. Also recognize that the relationship between the expected life of the pump, a , and its failure rate, λ , is

$$\lambda = \frac{1}{a} \quad (14.32)$$

Solution

With $t = 3a$ to express three times the pump's expected life,

$$P(T > 3a) = e^{-(1/a)(3a)} = e^{-3} = 0.0498 = 4.98\%$$

Therefore, there is a 5% chance that the pump will survive past three times its expected life.

To calculate the probability that a pump will survive at least five times its expected life, t is set to $5a$, and the aforementioned equation is solved as follows:

$$P(T > 5a) = e^{-(1/a)(5a)} = e^{-5} = 0.0067 = 0.67\%$$

Similarly, the probability that the pump will last at least 10 times its expected life is

$$P(T > 10a) = e^{-(1/a)(10a)} = e^{-10} = 4.54 \times 10^{-5} = 0.0045\%$$

As expected, the probability decreases *exponentially* with increasing survival time.

Illustrative Example 14.13

The concentration of a particular toxic substance in a wastewater stream in units of parts per million (ppm) is known to be normally distributed with mean $\mu = 100$ ppm and a standard deviation $\sigma = 2.0$ ppm. Calculate the probability that the concentration of this toxic material, c , is between 98 and 104 ppm.

Solution

Because c is normally distributed with $\mu = 100$ and the standard deviation $\sigma = 2.0$, a standard normal variable can be calculated as $(c - 100)/2$, and

$$P(98 < c < 104) = P\left(-1 < \left[\frac{c - 100}{2}\right] < 2\right) = P(-1 < Z < 2)$$

From the values in the standard normal table, Table 14.1:

$$P(98 < c < 104) = 0.341 + 0.477 = 0.818 = 81.8\%$$

Illustrative Example 14.14

The temperature of a polluted estuary during the summer months is normally distributed with mean of 56°F and standard deviation 3.0°F . Calculate the probability that the temperature is between 55°F and 62°F .

Solution

Normalizing the temperature, T , to a standard normal variable gives:

$$Z_1 = \frac{55^\circ\text{F} - 56^\circ\text{F}}{3.0^\circ\text{F}} = -0.333$$

$$Z_2 = \frac{62^\circ\text{F} - 56^\circ\text{F}}{3.0^\circ\text{F}} = 2.0$$

Thus,

$$\begin{aligned} P(-0.333 < Z < 2.0) &= P(0.0 < Z < 2.0) - P(0.0 < Z < 0.333) = 0.4722 \\ &\quad - 0.1293 = 0.6015 = 60.15\% \end{aligned}$$

Illustrative Example 14.15

The annual failure rate, Y , of a coolant recycle pump in a wastewater treatment plant has a log-normal distribution. If $\ln(Y)$ has a mean of 2.0 and variance, σ^2 , of 1.5, find $P(0.175 < Y < 1)$.

Solution

If Y has a log-normal distribution, $\ln(Y)$ has a normal distribution with $\mu = 2$ and $\sigma = 1.5^{1/2} = 1.22$. Therefore,

$$\begin{aligned} P(0.175 < Y < 1) &= P(\ln(0.175) < \ln(Y) < \ln(1)) \\ &= P\left(\left[\frac{\ln(0.175) - 2}{1.22}\right] < \frac{\ln(Y) - 2}{1.22} < \left[\frac{\ln(1) - 2}{1.22}\right]\right) \\ &= P(-3.07 < Z < -1.64) = 0.1587 - 0.0011 \\ &= 0.1576 = 15.76\% \end{aligned}$$

14.5 Weibull Distribution

Rather than following an exponential distribution, the failure rate of equipment frequently exhibits three distinct stages over time: a break-in stage with a declining failure rate, a useful life stage characterized by a fairly constant failure rate, and a wear out period characterized by an increasing failure rate. Many industrial parts and components follow this failure

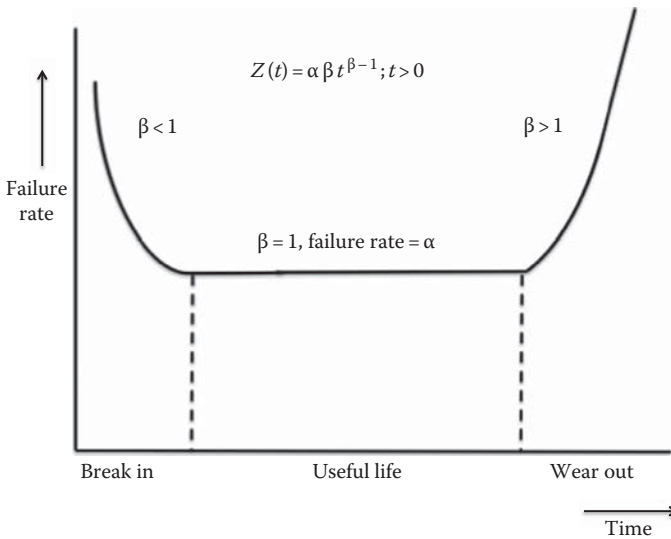


FIGURE 14.8
Bathtub curve represented by the Weibull distribution.

pattern. A failure rate curve exhibiting these three phases (see Figure 14.8) is called a *bathtub* curve.

Weibull introduced the distribution, which bears his name, principally on empirical grounds to represent certain life test data. The Weibull distribution provides a mathematical model of all three stages of the bathtub curve. An assumption about the *failure rate*, $Z(t)$, that reflects all three stages of the bathtub curve is:

$$Z(t) = \alpha \beta t^{\beta-1}, \quad t > 0 \quad (14.33)$$

where α and β are constants. For $\beta < 1$, the failure rate $Z(t)$ decreases with time. For $\beta = 1$, the failure rate is constant and equal to α . For $\beta > 1$, the failure rate increases with time. One can then show that the pdf of T , time to failure, for a Weibull distribution is [3]:

$$F(t) = \alpha \beta t^{\beta-1} e^{-\alpha t^\beta}, \quad t > 0, \alpha > 0, \beta > 0 \quad (14.34)$$

The variety of assumptions about failure rate and the probability distribution of time to failure that can be accommodated by the Weibull distribution make it especially attractive in describing failure time distributions in industrial and process plant applications.

To illustrate probability calculations involving the exponential and Weibull distributions, consider first the case of a transistor having a constant rate of

failure of 0.01/1000h. To find the probability that the transistor will operate for at least 25,000h, first note that:

$$Z(t) = 0.01$$

This ultimately provides:

$$f(t) = \exp\left(-\int_0^t 0.01 dt\right) = 0.01e^{-0.01t}, \quad t > 0$$

as the pdf of T , the time to failure of the transistor. Because t is measured in thousands of hours, the probability that the transistor will operate for at least 25,000h is given by:

$$P(T > 25) = \int_{25}^{\infty} -0.01e^{-0.01t} dt - e^{-\infty} + e^{-0.01(25)} = 0 + 0.78 = 0.78 = 78\%$$

Now suppose it is desired to determine the 10,000h reliability of a circuit of five such transistors connected in series. The 10,000h reliability of one transistor is the probability that it will last at least 10,000h. This probability can be obtained by integrating the pdf of T which gives

$$P(T > 10) = \int_{10}^{\infty} -0.01e^{-0.01t} dt = -e^{-\infty} + e^{-0.01(10)} = 0 + 0.90 = 0.90 = 90\%$$

This result also represents the *reliability* R , that the circuit will last at least 10,000h, that is, $R(10)=0.90$.

The 10,000h reliability of a circuit of five transistors connected in series is obtained by applying the formula for the reliability of series system to obtain:

$$R_s = [R(10)]^5 = (0.9)^5 = 0.59 = 59\%$$

Estimates of the parameters α and β in Equation 14.33 can be obtained by using a graphical procedure described by Bury [2]. This procedure is based on the fact that:

$$\ln\left[\ln\frac{1}{1-F(t)}\right] = \ln(\alpha) + \beta \ln(t) \quad (14.35)$$

where

$$F(t) = 1 - e^{-\alpha t^\beta}, \quad t > 0; F(t) = 0, \quad t < 0 \quad (14.36)$$

defines the cdf of the Weibull distribution. In Equation 14.33, the expression

$$\ln \left[\ln \frac{1}{1 - F(t)} \right] \quad (14.37)$$

represents a linear function of $\ln(t)$ with slope β and intercept $\ln(\alpha)$. The graphical procedure for estimating α and β on the basis of a sample of n observed values of t , time to failure, first involves the ordering of the observations from smallest ($i = 1$) to largest ($i = n$). The value of the i th observation varies from sample to sample. It can be shown that the average value of $F(t)$ for t equal to the value of the i th observation of T is $i/(n + 1)$. One may then plot

$$\ln \left[\ln \frac{1}{1 - (i/(n + 1))} \right] \quad (14.38)$$

against the natural logarithm of the i th observation for $i = 1$ to n . Under the assumption that T has a Weibull distribution, the plotted points lie on a straight line whose slope is β and whose intercept is $\ln(\alpha)$. Special Weibull probability paper allows plotting the i th observation against $i/(n + 1)$ to achieve the same result.

Illustrative Example 14.16

Assume the failure rate of a process can be described by a Weibull distribution. Obtain the probability equation if the failure rate is given by:

1. $Z(t) = t^{-0.25}$
2. $Z(t) = t^{-\sqrt{1/2}}$

Solution

For Case 1, from Equation 14.33 for $Z(t)$,

$$\beta - 1 = -0.25, \quad \beta = 1 - 0.25, \quad \beta = 0.75$$

Also from Equation 14.33,

$$\alpha\beta = 1, \quad \alpha(0.75) = 1, \quad \alpha = 1.33$$

For Case 2, from Equation 14.33 for $Z(t)$,

$$\beta - 1 = -\sqrt{1/2}, \beta = 1 - \sqrt{1/2} = 1 - 0.707, \beta = 0.293$$

and

$$\alpha\beta = 1, \alpha(0.293) = 1, \alpha = 3.41$$

Illustrative Example 14.17

The life (time to failure) of a machine component can be described using a Weibull distribution [2]. Determine the probability that the component lasts at least 25,000 h if t is measured in thousands of hours. Outline how to determine the probability that the component lasts a given period of time if the failure rate $Z(t) = t^{-1/2}$.

Solution

With the failure rate $Z(t) = t^{-1/2}$, Equation 14.33 can be used to determine the values of α and β as follows:

$$\beta - 1 = -1/2, \beta = 0.5$$

and

$$\alpha\beta = 1, \alpha(0.5) = 1, \alpha = 2$$

For these values of α and β , the Weibull pdf is:

$$f(t) = t^{-1/2} e^{-2t^{1/2}}, \quad t > 0$$

Integration of this pdf will yield the required probability. For this case, $t = 25$ with units of 1000 h, yielding the expression for the probability that the component lasts at least 25,000 h as:

$$P(T > 25) = \int_{25}^{\infty} t^{-1/2} e^{-2t^{1/2}} dt = -e^{-2t^{0.5}} \Big|_{25}^{\infty}$$

This may be integrated to give:

$$P(T > 25) = -0 - (-e^{-2(25)^{0.5}}) = 4.5 \times 10^{-5}$$

Illustrative Example 14.18

The life of an electronic component is a random variable having a Weibull distribution with $\alpha=0.025$ and $\beta=0.50$. What is the probability that the component will last more than 4000h?

Solution

The probability that the component will last more than 4000h is given by:

$$P(T > 4000) = \int_{4000}^{\infty} f(t) dt = \int_{4000}^{\infty} (0.025)(0.50)t^{0.50-1}e^{-0.025t^{0.5}} dt$$

$$P(T > 4000) = \int_{4000}^{\infty} (0.0125)t^{-0.50}e^{-0.025t^{0.5}} dt$$

$$P(T > 4000) = [-e^{-0.025t^{0.5}}]_{4000}^{\infty} = -0 - (-e^{-0.025(4000)^{0.5}})$$

$$P(T > 4000) = e^{-0.025(63.24)} = e^{-1.581} = 0.2057 = 20.57\%$$

Illustrative Example 14.19

The time in days to failure of each sample of 10 electronic components is observed as follows:

71, 40, 90, 149, 127, 53, 106, 36, 18, 165

Assuming a Weibull distribution applies, estimate the parameters α and β .

Solution

As noted earlier, the Weibull distribution parameters α and β are determined using a graphical procedure described by Bury [2]. First the observations are rank ordered from smallest to largest time to failure as follows:

18, 36, 40, 53, 71, 90, 106, 127, 149, 165

The natural log transform of these values are then computed and represent values of X . Values of Y are computed from corresponding values of $\ln\{\ln(1/(1-F(t)))\} = \ln\{\ln(1/(1-(i/n+1)))\}$. Table 14.4 was generated from these values of X and Y for this data set, and Figure 14.9 shows these data plotted in Excel for the determination of the regression coefficient values for determining values of α and β .

From Figure 14.9, the estimated value of β is 1.40, and the estimated value of $\ln(\alpha)$ is -6.428, making α equal to 0.0016.

TABLE 14.4
Data for Estimation of Weibull Parameters for Illustrative Example 14.19

Time to Failure, <i>t</i> (Days)	Order of Failure, <i>i</i>	ln(<i>t</i>)	$\ln \left[\ln \frac{1}{1 - (i/(n + 1))} \right]$
18	1	2.89	-2.35
36	2	3.58	-1.61
40	3	3.69	-1.14
53	4	3.97	-0.79
71	5	4.26	-0.50
90	6	4.50	-0.24
106	7	4.66	0.01
127	8	4.84	0.26
149	9	5.00	0.53
165	10	5.11	0.87

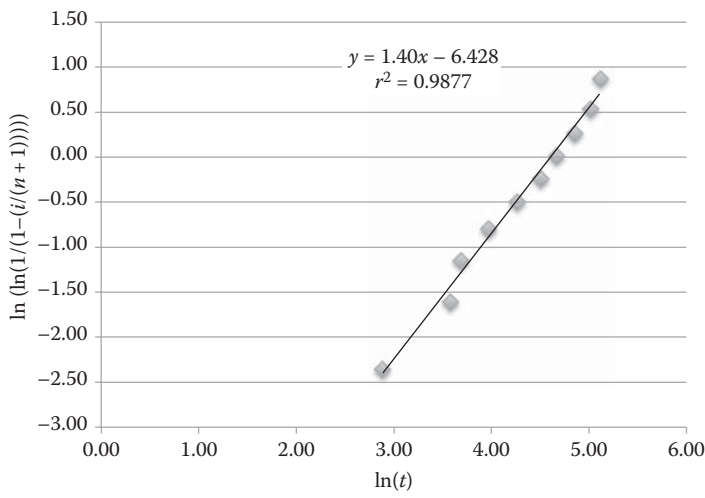




FIGURE 14.9
Illustrative Example 14.19 data plotting to determine Weibull distribution α and β values.

14.6 Fault Tree Analysis







A *fault tree* is a graphical technique used to analyze both rare and complex systems when data about the performance of these systems are not readily available. However, this method has been used extensively and has found numerous applications in the chemical process industries involving HZRA.

The objective of the fault tree method is to spotlight faulty conditions that cause a system to fail. FTA attempts to describe how and why an accident or another undesirable event has occurred. It may also be used to describe how and why an accident or other undesirable event could take place. In effect, FTA provides a method for determining causes of an accident. The analysis usually identifies equipment failures and/or human errors that can result during an accident. FTA also finds wide application in environmental management as it applies to HZRA and analysis of process and plant systems.

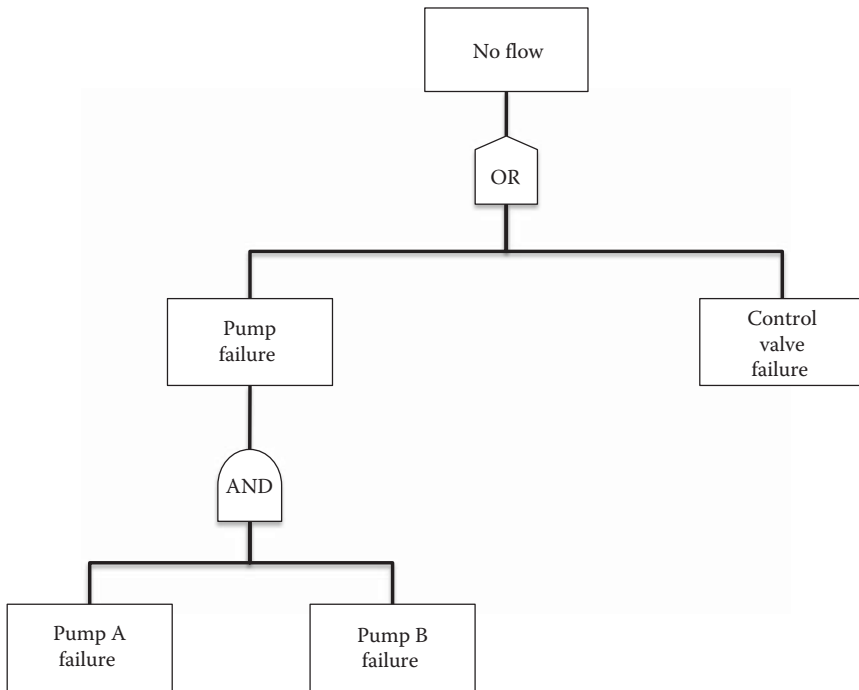
FTA seeks to relate the occurrence of an undesired event, the “top event,” to one or more antecedent events, called *basic events*. The top event may be, and usually is, related to the basic events via certain intermediate events. A fault tree diagram exhibits the causal chain linking the basic events to the intermediate events and the latter to the top event. In this chain, the logical connection between events is indicated by so-called *logic gates*. The principal logic gates are the “AND” gate, symbolized on the fault tree by  and the “OR” gate symbolized by . Additional symbols are provided in Table 14.5.

As a simple example of a fault tree, consider a water pumping system in a power plant consisting of two pumps A and B, where A is the pump ordinarily operating and B is a standby unit that automatically takes over if A

TABLE 14.5**Fault Tree Symbols**

Basic event	Standard usage: Basic initiating fault requiring no further development
	Modified ADL usage: Represents initiating event and therefore has a yearly rate of occurrence
Undeveloped event	Standard usage: Event which is not developed any further as it is not required or data are unavailable
	Modified ADL usage: Represents contributing events having taken place
External event	Standard usage: Event normally expected to occur
	Modified ADL usage: Not used as even events normally expected to occur can lead to an undesired outcome and data may not be any more accurate than for any other type of event
Intermediate event	Standard and ADL usage: Intermediate level event caused by more primary event developed below
	
AND gate	Standard and ADL usage: Logic gate where output fault occurs only if all input faults/events occur
	
OR gate	Standard and ADL usage: Logic gate where output fault occurs if at least one of the input faults/events occurs
	

ADL, alternate digital logic.

**FIGURE 14.10**

Fault tree for a water pumping system example.

fails. A control valve in both cases regulates flow of water through the pump. Suppose that the top event is no water flow, resulting from the following basic events: failure of pump A and failure of pump B, or failure of the control valve. The fault tree diagram for this system is shown in Figure 14.10. Additional fault trees can be found in Figures 14.11 and 14.12.

Finally, the reader should note the following properties of a fault tree:

1. A fault tree works backward from an undesirable event or ultimate consequence to the possible causes and failures.
2. It relates the occurrence of an undesired event to one or more preceding events.
3. It “chain-links” basic events to intermediate events that are, in turn, connected to the top event.
4. It is used in the calculation of the probability of the top event.
5. It is based on the most likely or credible events that lead to a particular failure or accident.
6. Its analysis includes human error as well as equipment failure.

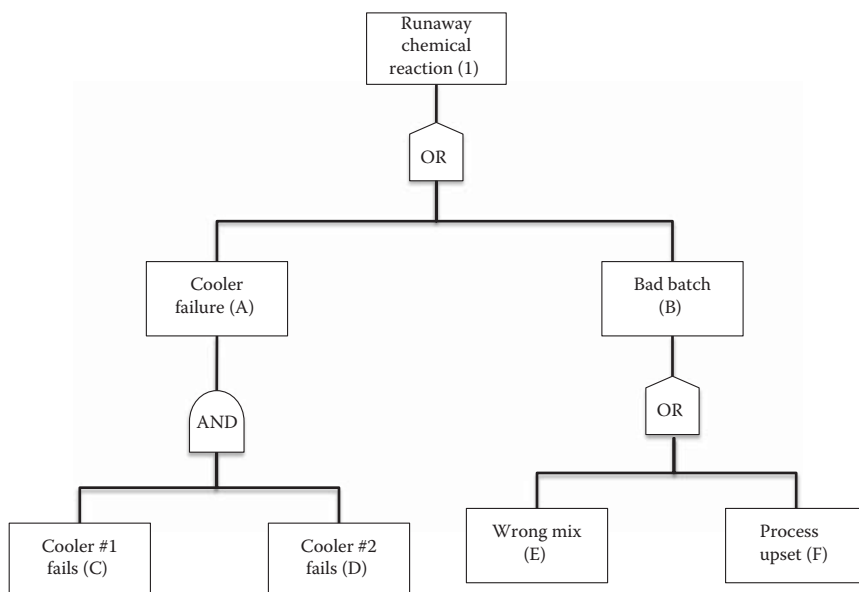


FIGURE 14.11
Fault tree with second branch.

Errors and uncertainties can occur in the FTA itself, and care should be taken to try to avoid the following during the FTA process:

1. Improperly identifying a hazard or hazards
2. Carrying out an FTA without a full understanding of the system being modeled
3. Using incorrect fault tree logic to describe a system failure
4. Not properly accounting for all failures
5. Not properly accounting for all failure causes

Illustrative Example 14.20

Refer to Figure 14.12. Calculate the probability of a runaway chemical reaction occurring in a year's time given the following probabilities from the plant engineer:

$$P(C)=0.05, P(D)=0.08, P(F)=0.06, P(G)=0.03, P(H)=0.01$$

Solution

Redraw Figure 14.12 and insert the given probabilities (see Figure 14.13). Calculate the probability that the runaway reaction will occur:

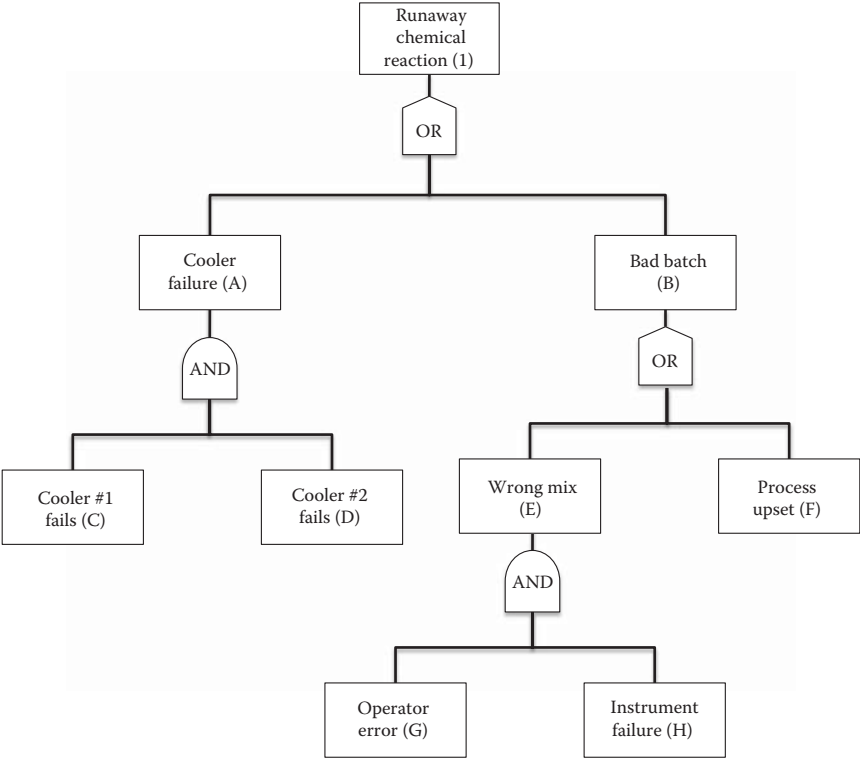


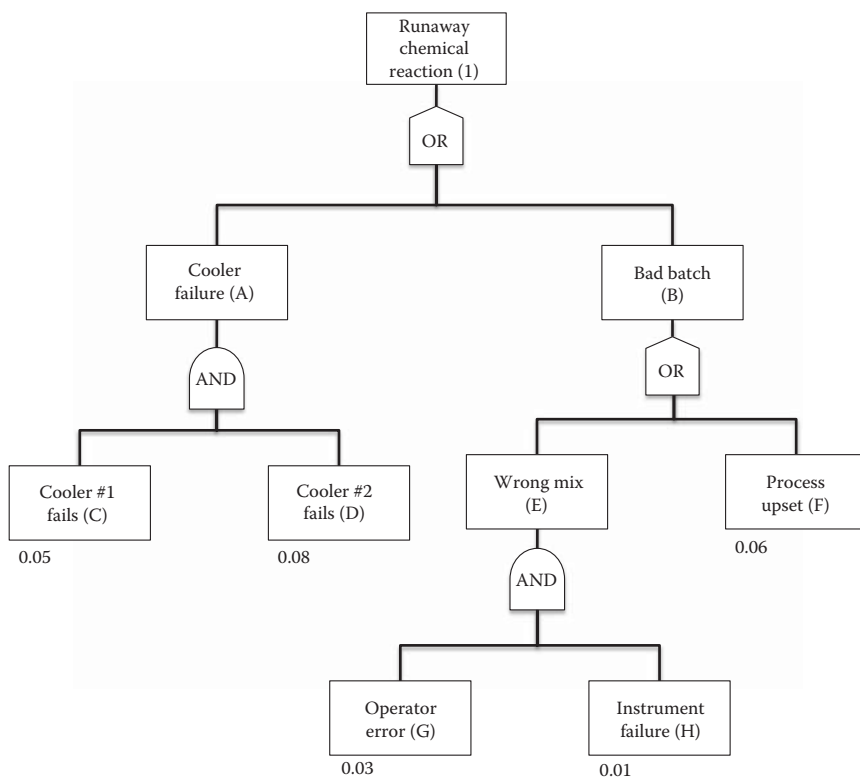
FIGURE 14.12
Fault tree with third branch.

$$P = (0.05)(0.08) + (0.01)(0.03) + 0.06 = 0.0040 + 0.0003 + 0.06$$
$$= 0.064 = 6.4\%$$

Note that the process upset, *F*, is the major contributor to the failure probability.

Illustrative Example 14.21

A distillation column explosion can occur if the overhead unit fails (OUC) or if there is a problem with the reboiler (RB). The overhead unit fails (OUC) only if both the cooler fails (OC) and the condenser fails (CO). Reboiler problems develop if there is a power failure (PF) or there is a failed tube (FT). A power failure occurs only if there are both operator error (OE) and instrument failure (IF). Construct a fault tree describing these failure modes. If the following annual probabilities are provided by the plant engineer, calculate the annual probability of a distillation column explosion at this plant:

**FIGURE 14.13**

Fault tree for runaway chemical reaction with probabilities for Illustrative Example 14.20.

$$P(\text{OC}) = 0.02, P(\text{CO}) = 0.05, P(\text{FT}) = 0.04, P(\text{OE}) = 0.60, P(\text{IF}) = 0.005$$

Solution

The fault tree is given in Figure 14.14. Based on the data provided,

$$\begin{aligned}
 P(\text{explosion}) &\approx (0.02)(0.05) + (0.005)(0.6) + 0.04 \approx 0.01 + 0.003 \\
 &+ 0.04 \approx 0.0413 \approx 4.13\%
 \end{aligned}$$

Note that the major contributor to an explosion at this facility is the failed tube (FT), whose probability is 0.040.

Illustrative Example 14.22

Consider the fault tree in Figure 14.15 for a flammable storage tank fire. Identify whether the numbered boxes should be AND or OR gates.

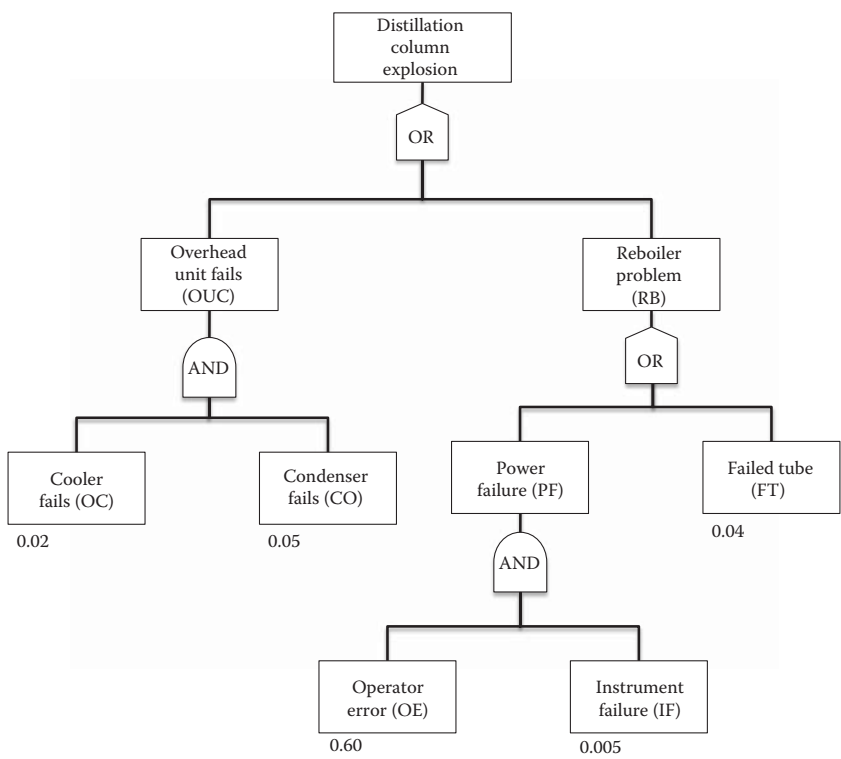


FIGURE 14.14
Fault tree for distillation column explosion with probabilities for Illustrative Example 14.21.

Solution

The numbered boxes in Figure 14.15 are described as follows:

1. For a flammable storage fire to occur, excess flammable vapor and air/O₂, and a source of ignition must be present. Therefore, Box 1 is an AND gate since all situations must occur.
2. For excess flammable vapor to occur, either a large leak in flammable containers or inadequate ventilation must be present. Therefore, Box 2 is an OR gate since only one situation need occur for excess flammable vapor to occur.
3. For a source of ignition to occur, there must be an open flame or an electrical ignition or a mechanical ignition must be present. Therefore, Box 3 is an OR gate since only one situation need occur to provide a source of ignition.

Illustrative Example 14.23

Briefly discuss staffing and cost requirements for an FTA.

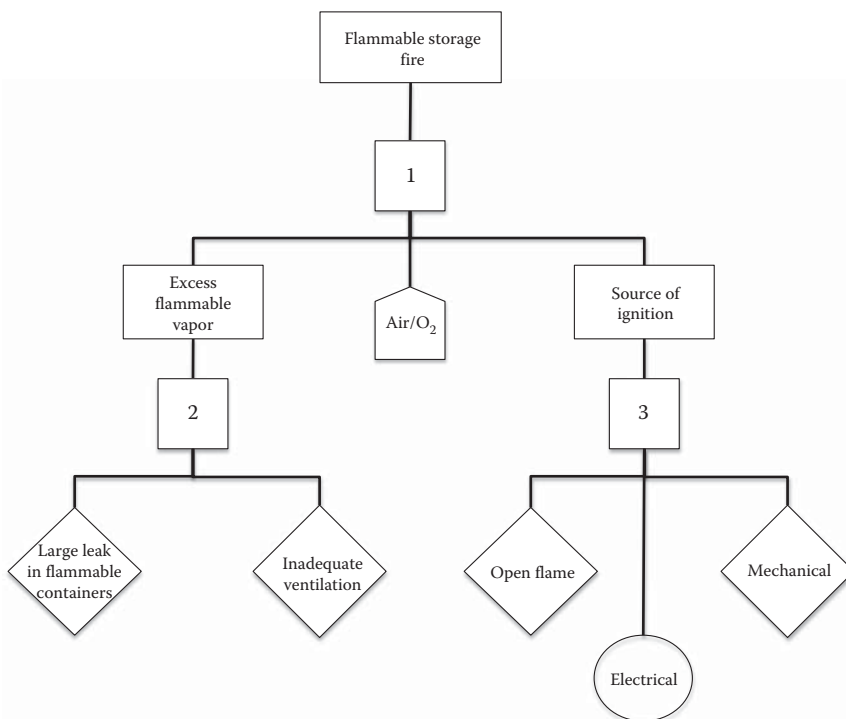


FIGURE 14.15
Fault tree for Illustrative Example 14.22.

Solution

Normally, a single person can do the FTA. The analyst should create a fault tree based on consultation with operators and engineers along with other personnel who are familiar with the equipment/systems that are being analyzed. By having one person creating the fault tree, there is continuity in the analysis. The analyst must have full and complete access to all figures necessary to define faults and failures that may contribute to an accident. If many fault trees are to be created, a team approach may be used. Here, each member of the team should concentrate on a single fault tree. Members of the team must work together along with other plant personnel to thoroughly complete the analysis.

The complexity of the system directly affects the time and cost requirements for the FTA. The more complex the system being analyzed, the larger the modeling processes and the longer the time needed to develop a solution to the analysis. Complex systems mean many potential events contributing to a range of accidents, resulting in larger and more complex fault trees, and longer and more complex analysis.

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15

Hazard/Event Consequences

15.1 Introduction

Consequences of accidents can be classified qualitatively by the degree of severity. Factors that help to determine the degree of severity are the concentration at which the hazard is released, the relative toxicity of the hazard, and, in the case of a chemical release, the length of time that a person is exposed to the hazardous agent. From a qualitative perspective, the worst-case consequence of a scenario is defined as a conservatively high estimate of the severity of the accident identified [1]. On this basis, one can qualitatively rank the consequences of accidents into *low*, *medium*, and *high* degrees of severity [2]. A low degree of severity means that the hazard consequence is nearly negligible, and the injury to persons, property, or the environment may be observed only after an extended period of time. The degree of severity is considered to be medium when the accident is serious but not catastrophic. An example of this could include a case where there is a release of a low concentration of a chemical that is considered to be highly toxic. Another example of a medium degree of severity could be a highly concentrated release of a less toxic chemical, large enough to cause injury or death to persons and damage to the environment unless immediate action is taken. There is a high degree of severity when the accident is catastrophic or the concentrations and toxicity of a chemical hazard are large enough to cause injury or death to many individuals, and there is long-term damage to the surrounding environment.

Potential consequences of other specific hazard/accident conditions can include:

1. Flying shrapnel
2. Rocketing tank parts
3. Fireballs created by mechanically atomized drops of burning liquid and vapor
4. Secondary fires and explosions caused by flaming tank contents
5. Release of toxic or corrosive substances to the surroundings

This chapter addresses the third step of the hazard risk assessment (HZRA) process (see Figure 7.2), i.e., hazard/event consequences. Several illustrative examples that follow detail how the calculations associated with this step are implemented. Perhaps the key to determining the consequences of an accident is the study of accident minimization/prevention. This topic and a host of others related to hazard/event consequence analysis are also covered in this chapter. The subject matter includes:

- Accident minimization/prevention
- Consequence estimation
- Failure modes, effects, and criticality analyses (FMECA)
- Vulnerability analysis
- Event tree analysis (ETA)

Because of the importance of ETA in the consequence step of HZRA, a short introduction to this topic follows.

Event trees are diagrams that evaluate the consequences of a specific hazard. The safety measures and the procedures designed to deal with the event are highlighted in this chapter. The consequences of each specific event that lead to the accident are also presented. An event tree is drawn (sequence of events that lead up to the accident). The accident is first described. This allows the path of the accident to be traced. It shows possible outcomes that could have arisen had a single event in the sequence been changed. Thus, an event tree provides a diagrammatic representation of event sequences that begin with the so-called initiating event and terminate in one or more undesirable consequences. In contrast to a *fault tree*, which works *backward* from an undesirable consequence to possible causes, an event tree works *forward* from the initiating event to possible undesirable consequences. As described earlier in Chapters 13 and 14, the initiating event may be equipment failure, human error, power failure, or some event that has the potential for adversely affecting an ongoing process.

15.2 Accident Minimization/Prevention

The first step in minimizing accidents and/or eliminating/reducing potential consequences in a chemical plant is to evaluate the facility for potential fires, explosions, and vulnerability to other hazards, particularly those of a chemical nature. This calls for a detailed study of the plant site and layout, materials, processes, operations, equipment, and training, plus an effective loss prevention program. The technical nature of industry requires detailed data and a broad range of experience to conduct this vulnerability and

accident prevention analysis effectively. This complex task, becoming more and more important in plant design today, is facilitated by available safety codes, standards, and practice information. The technical approach to evaluating the consequences of hazards is discussed later in this chapter.

A good design (particularly as applied to a plant) should:

1. Be intrinsically safe
2. Have adequate design margins
3. Ensure sufficient system reliability
4. Include fail-safe controls
5. Provide for fault detection and alarms
6. Incorporate protection instrumentation

Coordinating safety engineering and industrial standards is principally the responsibility of the American National Standards Institute (ANSI), a federation of industrial companies, government agencies, trade organizations, technical societies, and consumer organizations. Burklin [3] cites the following National Fire Protection Association (NFPA) definitions of the types of document that have been developed to ensure safety in design:

1. *Code*. A code is a document containing only mandatory provisions using the word "shall" to indicate requirements. Explanatory material is only included in notes, footnotes, or an appendix.
2. *Standard*. This is a document containing both mandatory provisions ("shall" rules) and advisory provisions ("should" recommendations).
3. *Recommended practice*. This term describes a document containing only advisory provisions using the word "should."
4. *Manual*. A manual is a document that is informative in nature and does not contain requirements or recommendations.

Table 15.1 lists the major organizations providing these documents. Table 15.2 is a cross-reference to the same information listing the design areas. An extremely useful and detailed description of these organizations is provided by Burklin [3].

The most logical starting point in the safety design approach is to select a site where the number of undesirable weather and topographic conditions is limited. Adequate utilities and support systems, plus fire protection services, are also required for a safe environment. Several earlier chapters presented information on plant site selection and layout. These features will now be considered from a safety point of view. The following guidelines should be observed in selecting a site that is favorable for the efficient and economical operation of a process in order to eliminate/reduce potentially important adverse consequences.

TABLE 15.1
Major Organizations Providing Codes and Standards, Recommended Practices, Design Criteria, or Guidelines for Equipment in Chemical and Allied Industry Process Plants

Organization	Organization Abbreviation
<i>Technical and Trade Groups</i>	
Air Conditioning & Refrigeration Institute	ARI
Air Moving and Conditioning Association	AMCA
American Association of Railroads	AAR
American Gas Association	AGA
American Petroleum Institute	API
American Water Works Association	AWWA
Chemical Manufacturers Association (formerly Manufacturing Chemists Association)	CMA
Chlorine Institute	CI
Compressed Gas Association	CGA
Cooling Tower Institute	CTI
Manufacturers Standardization Society	MSS
National Electrical Manufacturers Association	NEMA
Pipe Fabrication Institute	PFI
Scientific Apparatus Makers Association	SAMA
Society of the Plastics Industry	SPI
Steel Structure Painting Council	SSPC
Tubular Exchanger Manufacturers Association	TEMA
<i>U.S. Government Agencies</i>	
Bureau of Mines	BM
Department of Transportation	DOT
U.S. Coast Guard	USCG
Hazardous Materials Regulation Board	HMRB
Federal Aviation Administration	FAA
Environmental Protection Agency	EPA
National Bureau of Standards	NBS
Occupational Safety and Health Administration	OSHA
<i>Testing Standards and Safety Groups</i>	
American National Standards Institute	ANSI
American Society for Testing and Materials	ASTM
National Fire Protection Association	NFPA
Underwriters Laboratories, Inc.	UL
National Safety Council	NSC

(continued)

TABLE 15.1(continued)

Major Organizations Providing Codes and Standards, Recommended Practices, Design Criteria, or Guidelines for Equipment in Chemical and Allied Industry Process Plants

Organization	Organization Abbreviation
<i>Insuring Associations</i>	
American Insurance Association	AIA
Factory Insurance Association	FIA
Factory Mutual System	FM
Oil Insurance Association	OIA
<i>Professional Societies</i>	
American Conference of Governmental Industrial Hygienists	ACGIH
American Industrial Hygiene Association	AIHA
American Institute of Chemical Engineers	AIChE
American Society of Mechanical Engineers	ASME
American Society of Heating, Refrigeration, and Air-Conditioning Engineers	ASHRAE
Illuminating Engineering Society	IES
Institution of Chemical Engineers (Britain)	ICHE
Institute of Electrical and Electronics Engineers	IEEE
Instrument Society of America	ISA

1. A fairly level site is needed to prevent spills (e.g., flammable liquids) from flowing. Slight inclines may be useful for drainage purposes. Firm soil well above the water level is also necessary.
2. Adequate water supplies for fire protection are vital. Other utility services, such as electricity, must be reliable and well maintained during emergencies. Plants depending on outside electricity should have two separate feeder circuits whenever possible, and possible failures of these utilities should be evaluated before construction. When one system fails, the other system must provide suitable switching or shutdown to prevent serious hazards.
3. Roadways should allow easy approach of emergency vehicles.
4. Sites near existing plants containing hazardous materials and near congested communities should be avoided.
5. Waste disposal systems containing flammable, corrosive, or toxic materials should be at least 250 ft from plant equipment.
6. Climate and natural hazards should be evaluated. Lightning arrestors should be installed to prevent lightning from directly striking flammable areas. Temperatures must be considered for outdoor operations.

TABLE 15.2

Areas Covered by Codes, Standards, Recommended Practices, Design Criteria, or Guidelines of Designated Organization

Design Area	Organization^a
Accident case history	ACA, AIA, AIChE, API, FIA, FM, NFPA, NSC, OIA, OSHA, USCG
Air compressors	AIA, ANSI, FM, USCG
Air-fin coolers	ARI, ASURAE, OIA, USCG
Boilers	ANSI, NFPA, NSC, UL
Combustion equipment and controls	ANSI, FIA, FM, NEPA, NSC, OIA, UL, USCG
Compressors	AIA, ARI, ASHRAE, ASME, FM, OIA, USCG
Cooling towers	M, FM, NFPA, OIA
Drain and waste systems	AIChE, AWWA, CMA, USCG
Dust collection equipment	FIA, FM, NFPA, USCG
Dust hazards	ACGIH, AIHA, ANSI, BM, FIA, FM, NFPA, NSC, UL, USCG
Electric motors	ANSI, CMA, IEEE, NFPA, UL, USCG
Electrical area classification	AIA, ANSI, API, CMA, FIA, FM, NFPA, NSC, OIA, OSHA, USCG
Electrical control and enclosures	AIA, ANSI, ARI, CMA, FIA, FM, IEEE, ISA, NEMA, NFPA, NSC, OIA, OSHA, UL, USCG
Emergency electrical systems	AGA, AIA, FM, IEEE, NEMA, NFPA, USCG
Fans and blowers	ACGIH, AIHA, AMCA, ARI, ASME, FM, USCG
Fire protection equipment	AIA, ANSI, API, AWWA, BM, CGA, CMA, FIA, NEMA, NFPA, NSC, OIA, OSMA, UL, USCG
Fire pumps	ANSI, FM, IEEE, NFPA, UL, USCG
Fired heaters	ANSI, ASME, FIA, FM, NFPA, OIA, UL, USCG
Gas engines	FM, NFPA, OIA, USCG
Gas turbines	AGA, FIA, FM, NFPA, OIA, USCG
Gear drives, power transmission	AIA, ANSI, NSC, USCG
Grounding and static electricity	AIA, ANSI, API, FIA, FM, IEEE, NEMA, NFPA, NSC, OIA, OSHA, UL, USCG
Inspection and testing	AIChE, AMCA, API, ASHRAE, ASTM, AWWA, CGA, CM, DOT, IEEE, MSS, NFPA, NSC, PFI, USCG
Instrumentation	AIA, ANSI, API, ARI, ASTM, AWWA, CGA, FIA, FM, HMRB, IEEE, ISA, NBS, NFPA, OIA, SAMA, UL, USCG
Insulation and fireproofing	AIA, ANSI, ASHRAE, ASTM, FM, OIA, UL, USCG
Jets and ejectors	USCG
Lighting	ANSI, FM, IEEE, IES, NEMA, NFPA, NSC, UL, USCG
Lubrication	AMCA, ANSI, ASME, NFPA
Material handling	MCA, NFPA, NSC, OSHA
Materials of construction	AIA, ANSI, ASTM, AWWA, CGA, CMA, CI, CTI, FM, HMRB, ISA, NBS, NFPA, NSC, OIA, TEMA, UL, USCG

(continued)

TABLE 15.2 (continued)

Areas Covered by Codes, Standards, Recommended Practices, Design Criteria, or Guidelines of Designated Organization

Design Area	Organization ^a
Noise and vibration	AGA, AIChE, AIUA, AMCA, ANSI, API, ARI, ASHRAE, ASTM, EPA, ISA, NFPA, NSC, OSHA, UL
Painting and coating	AIChE, ANSI, ASTM, AWWA, HMRB, OSHA, NBS, SSPC, UL
Piping materials and systems	AGA, AIA, ANSI, API, ARI, ASHRAE, ASTM, AWWA, CGA, CI, FIA, FM, HMRB, IES, MSS, NBS, NFPA, NSC, PFI, SPI, UL, USCG
Plant and equipment layout	AAR, AIA, API, AWWA, CGA, CMA, FIA, FM, HMRB, NFPA, NSC, OIA, USCG
Pneumatic conveying	ANSI, NFPA, USCG
Power wiring	ANSI, API, FIA, FM, IEEE, NEMA, NFPA, OIA, OSHA, UL, USCG
Pressure relief equipment systems	AIA, API, ASME, CGA, CI, FIA, FM
Pressure vessels	AIA, API, ASME, CGA, DOT, NFPA, NSC, OSHA, HMRB, OIA, OSHA, USGC
Product storage and handling	AAR, AIA, AIChE, ANSI, API, CCA, CI, CMA, FIA, FM, NFPA, OIA, OSHA, USCG
Pumps	AIChE, ANSI, AWWA, CI, NFPA, OIA, UL, USCG
Refrigeration equipment	ANSI, API, ASHRAE, FM, NFPA, UL, USCG
Safety equipment	ACGIH, AIHA, ANSI, BM, CGA, CI, CMA, FM, NSC, OSHA, UL, USCG
Shell and tube exchangers	AGA, AIChE, API, ASHRAE, ASME, CGA, PFI, USCG
Shutdown systems	ATA, API, FIA, NFPA, OIA, UL, USCG
Solids conveyors	CMA
Stacks and flares	FAA, OIA, USCG
Steam turbines	AIA, FM, IEEE, OIA, USCG
Storage tanks	AWWA, CI, NBS, NFPA, OIA, OSHA, UL, USCG
Ventilation	ACGIH, AIHA, ANSI, BM, FIA, FM, NFPA, NSC, UL, USCG
Venting requirements	API, FIA, FM, HMRB, NFPA, USCG

Source: Burklin, C., *Chem. Eng.*, 79, 56, 1972. With permission.

^a See Table 15.1 for abbreviations.

7. Providers of emergency services, such as the fire department, should be well trained and well equipped, and be able to respond rapidly.

Plant layout should be planned to provide efficient operation, proper working conditions, constant flow of materials, inventory control, and mechanisms for ensuring safety. Plant site and plans for future expansion are also considerations. Congestion and concentration of operations should be covered in the initial evaluation to determine that the control of fires, explosions, toxic chemical releases, and environmental hazards will be possible.

Localizing such accidents may minimize the damage and permit control of the hazard. Guidelines for a general layout are as follows:

1. Process units, especially critical equipment and storage areas, should be adequately spaced. When this is impossible, barricades, fire protection units, and protective construction should be provided.
2. A rectangular block layout should be followed to provide adequate roadways between process equipment for emergency vehicle access and minimize the spread of fire.
3. The water system layout should provide an adequate supply to all areas of the plant. Piping, pumps, tanks, valves, hydrants, and auxiliary equipment should follow acceptable standards.
4. Utilities should be protected by dual supplies.
5. Offices, the cafeteria, laboratories, and other populated places should be located on the periphery of the site (displaced from hazardous areas) and *upwind* from stacks and the center of the plant.
6. Storage, loading, and transportation facilities should also be located on the periphery of the plant to minimize traffic through operating areas.
7. Waste disposal should be located *downwind* to minimize exposure to plant workers and the community.
8. Sewers and drains should provide safe and efficient removal of liquids. The drainage system must provide sufficient capacity to prevent any likely flooding from severely damaging equipment.
9. Fire protection equipment and emergency facilities must be readily available and sufficient.
10. Plant security must provide efficient supervision of plant boundaries and entrances.

To contain the hazards in a critical area, process units should in general be located in the same vicinity instead of scattered throughout the plant. Spacing requirements of the units are determined by:

1. Fire, explosion, and other hazards of the process and the nature of the materials
2. The quantity of materials contained in any one unit or area
3. The possibility of equipment damage from exposure to potential nearby fires, explosions, and other hazards
4. The value of the area
5. The importance of the unit to the continuity of production
6. The availability of adequate firefighting and rescue operations
7. The climate and topographical conditions

Chemical plants also consist of process buildings, storage and warehouse buildings, control houses, laboratories, and general offices. Depending on the nature of the activity and the quality of the contents, the structural requirements and protection features will vary. Building standards are defined by the National Code of the American Insurance Association and should be consulted for specific details regarding building structural requirements.

Buildings erected must be adequate with respect to ventilation, explosion venting, firewalls, exits, drainage, and electrical wiring. The safety of the equipment and the structures is often a function of their age, and the degree of "adequacy" must be evaluated based on this as well as the aforementioned factors.

The equipment and systems of the processing plant are designed to contain the chemicals under processing conditions and to provide the controlled environment required for production. This equipment is designed to function under both specific process conditions and upset conditions. Upset conditions that should be considered in design include fires, explosions, and accidental chemical releases.

A well-designed piece of equipment has safety and loss prevention features built into it. The following typical equipment design considerations are important from the standpoint of loss prevention:

1. Reliability of the unit
2. Ease of operation
3. Flexibility of the unit
4. Amenability to future expansion
5. Provisions for inspection and maintenance
6. Adequate emergency shutdown facilities
7. Standardization of equipment for rapid replacement
8. Design to anticipate pressure ranges with overpressure controls
9. Design to anticipate temperature ranges with overtemperature controls

Equipment should be checked for the following:

1. Compliance with existing recognized good industry practices, safety codes, standards, and governmental regulations
2. Construction according to specifications
3. Operation without undue strain on the operator
4. Reliable operation under all situations, including a difficult startup and shutdown
5. Provision of adequate safeguards and protection equipment
6. An inspection and maintenance program sufficient to provide reliable operation

The factors that enter into the design of vessels include type of material, configuration, method of construction, design stresses, and thickness of the metal. As with any equipment, design pressures and temperatures should take into consideration the most severe combination of conditions anticipated. Vessels must be completely drainable. Liners and wear plates may be required to prevent corrosion. Vessels should also be provided with overpressure protection as required. Vents and relief valve vent piping should be so arranged that the vented vapors do not constitute a hazard. Relief valves must be kept free from corrosion or fouling and should be operable at all times.

All pressure vessels should be tested, inspected, and marked in accordance with code requirements. Further inspection of field fabrication vessels may include the radiography of all seams and other pertinent tests.

Standards and codes have very specific safety requirements for the design of tanks for flammable liquids or gases and pressurized chemicals such as ammonia. Overpressure devices and vents should be included in the design. Tank and vessel supports should be built for the maximum intended load.

Mixers and agitators designed for flammable liquids or dusts should be constructed to minimize fire and explosion possibilities. Electrical equipment should follow the requirements of the National Electrical Code. Equipment should be grounded to prevent the accumulation of static electricity.

The most common heat transfer unit in the chemical process industry is the tubular (tube and bundle/shell and tube) heat exchanger. Tube materials must be selected to resist corrosion and fouling. Whenever a heat exchanger services a normal or an emergency cooling facility, it is recommended that its reliability as well as the adequacy of the supply of the coolant be evaluated. Reactive heat exchanger fluids require carefully engineered units to ensure containment. Interlocking of agitation equipment and heat exchangers is also necessary. Adequacy of controls and instrumentation is vital in the area of temperature control. Heat exchangers should be equipped with relief valves, bypass piping, and adequate drains. To prevent tube leakage or rupture, only seamless tubes should be used. Heat exchanger tubes and piping should also be designed to withstand thermal expansion and contraction to prevent excessive stress on connections [4].

Pumps, compressors, turbines, drivers, and auxiliary machinery should be designed to provide reliable, rugged performance. Pump selection and performance depend on the capacity required and the nature of the fluids involved. Remotely controlled power switches and shutoff valves are necessary to control fluid flow during an emergency. The inlets for air compressors should be strategically located to prevent the intake of hazardous materials [5].

All piping, valves, and fittings should be designed according to recognized standards for the working pressures and structural stresses anticipated. The piping should be well supported and protected against physical and mechanical damage. Piping systems should be located in serviceable areas. Nondestructive testing in the field, such as ultrasonic, radiographic, or eddy current examination, is preferred to the spot-checking of batches of pipes and tubes by destructive means at the point of manufacture.

Evaluation of piping networks should be oriented toward the elimination of unnecessary pipe runs transporting hazardous materials. Pipelines should contain a sufficient number of well-placed valves to control the flow of fluids during fire emergencies. Piping should be color coded for rapid identification; the diamond symbol used in the National Fire Protection Association's System 704 for fire hazard information of materials may also be appropriate for proper pipe labeling [3].

Piping should also be arranged to allow the shortest, most direct route without congestion. They should be installed to prevent the trapping of liquids and should contain adequate valving and provisions for contraction and expansion. Joints must be properly welded and secured.

Good foundations assure stability of the equipment. The foundation should extend below the soil frost line to eliminate settling and shifting of equipment. Major loads and equipment producing vibrations (e.g., pumps) should not be placed on filled ground. High towers and major vessels should have properly installed anchor bolts.

The reader may choose to return to Chapter 13 to review the material presented there on this topic.

Illustrative Example 15.1

Describe how the consequences of an accident at home could be minimized or eliminated.

Solution

Some possible ways to minimize the consequences of accidents in the home are listed below:

1. All appropriate emergency services (police, fire department, ambulance, and poison control) should be listed by the phone.
2. Fire extinguishers should be available and easily accessible to areas where they are mostly likely to be needed (kitchen, garage, and workshop).
3. Fire drills should be planned and practiced.
4. Childproofing (cabinet hooks, plastic electrical outlet plugs, etc.) should be carried out in homes with children, grandchildren, etc.
5. Carpeting should be secured in place to prevent tripping.

Illustrative Example 15.2

A baghouse has been used to clean a metal-laden particulate gas stream for nearly 30 years. There are 600, 8 in. diameter bags in the unit. A total of 50,000 acfm of gas at 250°F enters the baghouse with a loading of 5.0 grains/ft³. The outlet loading is 0.3 grains/ft³. Local EPA regulations state that the maximum allowable outlet loading is 0.4 grains/ft³. If the system operates at a pressure drop of 6 in. H₂O, how many bags can fail before this consequence leads to the unit being out of compliance? The Theodore–Reynolds equation (see the following) applies and all the contaminated gas emitted through the broken bags may be assumed to be the same as that passing through the tube sheet thimble.

The effect of bag failure on baghouse fractional penetration, P (or 1-fractional efficiency, E), can be described by the following equations [4]:

$$P_t^* = P_t + P_{tc} \quad (15.1)$$

$$P_{tc} = \frac{0.582(\Delta P)^{1/2}}{\phi} \quad (15.2)$$

$$\phi = \frac{q}{[LD^2(T + 460)^{1/2}]} \quad (15.3)$$

where

P_t^* is the penetration after bag failure

P_t is the penetration before bag failure

P_{tc} is the penetration correction term, i.e., the contribution of broken bags to P_t^*

ΔP is the pressure drop, in. H₂O

ϕ is the dimensionless parameter defined by Equation 15.3

q is the volumetric flow rate of contaminated gas, acfm

L is the number of broken bags

D is the bag diameter, in.

T is the temperature, °F

For a detailed development of the aforementioned equation, refer to Reynolds, Jeris, and Theodore [5].

Solution

Calculate the efficiency, E , and penetration, P , before the bag failures:

$$E = \frac{\text{Inlet loading} - \text{Outlet loading}}{\text{Inlet loading}}$$

$$E = \frac{5.0 - 0.03 \text{ grains / ft}^3}{5.0 \text{ grains / ft}^3} = 0.9940 = 99.40\%$$

$$P_t = 1 - 0.9940 = 0.0060 = 0.60\%$$

Calculate the efficiency and penetration, P_t^* , based on regulatory conditions:

$$E = \frac{5.0 - 0.4 \text{ grains / ft}^3}{5.0 \text{ grains / ft}^3} = 0.9200 = 92.00\%$$

$$P_t^* = 1 - 0.92 = 0.08 = 8.0\%$$

Calculate the penetration term, P_{tc} , associated with the failed bags using Equation 15.1:

$$P_{tc} = P_t^* - P_t = 0.08 - 0.006 = 0.0740$$

Substituting the expression for ϕ from Equation 15.3 into the equation for P_{tc} and solving for the number of failed bags, L yields

$$L = \frac{qP_{tc}}{[(0.582)(\Delta P)^{0.5}(D)^2(T + 460)^{0.5}]}$$

The number of bag failures that the system can tolerate and still remain in compliance is then determined by substitution to yield

$$L = \frac{(50,000 \text{ acfm})(0.074)}{[(0.582)(6)^{0.5}(8)^2(250 + 460)^{0.5}]} = 1.52$$

Thus, if two bags fail, the resulting consequence is that the baghouse is out of compliance.

Illustrative Example 15.3

Comment on the result of the previous illustrative example.

Solution

The importance of when to replace a broken bag will depend on the type of collector and the resultant effect on outlet emissions. In “inside bag collection” types of collectors, it is very important that dust leaks be stopped as quickly as possible to prevent adjacent bags from being abraded by jet streams of dust being emitted from the broken bag.

This is called the “domino effect” of bag failure. “Outside bag collection” systems do not have this problem, and the speed of repair is determined for these systems by whether the outlet emissions have exceeded their limit. Often, it will take several broken bags, as the previous example indicates, to create an emission problem, and a convenient maintenance schedule can be employed instead of emergency maintenance.

15.3 Consequence Estimation

For any specific incident, there can be an infinite number of incident outcome cases that can be considered. There is also a wide range of consequence models that can be applied. It is important, therefore, to understand the objectives of a given study in order to limit the number of incident outcome cases to those that satisfy those state objectives. Following is an example of variables that can be considered for an accidental release/emission scenario [5]:

1. Quality, magnitude, and duration of the release
2. Dispersion parameters (wind speed, wind direction, and weather stability conditions)
3. Flammable releases and ignition possibility (ignition sources/location and ignition strength)
4. Energy levels contributing to explosive effects (if applicable)
5. Impact of release on people, property, or the environment via thermal radiation, projectiles, shock-wave overpressure, toxic dosage, etc.
6. Mitigating effects including safe havens, evacuation opportunities, daytime/nighttime population differences, etc.

Following an accident, the consequence effects on individuals able to escape or remain in a shelter (or equivalent) differ from those for people in the open. Factors to consider in relation to building types and human behavior include the following:

1. *The nature of the hazard considering both intensity and duration.* Shelters vary in the degree of protection provided. For thermal and toxic hazards, shelters can have a beneficial effect. However, for explosions, the hazard may be greater within a shelter because of the possibility of the building collapsing.
2. *The nature of the hazard considering its degree of toxicity and its warning properties.* A release of carbon monoxide provides no warning while

a release of an amine normally provides a strong odor warning at concentrations well below the harmful levels.

3. *The nature of the surrounding population.* The distribution of the population indoors generally varies depending on the time of day and the season, as well as the overall health of the population (senior citizens, infirm, etc.). The type of clothing (cotton, wool, polyester, etc.) worn by the population exposed to a thermal stress from a fire or explosion can impact the resultant consequence of this exposure.
4. *The type of buildings and their construction.* Building factors can include ventilation rates, resistance to blast effects, the ability of overhead fixtures to remain intact, etc.
5. *The effectiveness of training and the availability of equipment for emergency response and medical treatment.* This applies to both the plant and emergency response services in the adjacent community. Trained personnel obviously can improve the chance of survival for those exposed.
6. *The prevailing weather conditions, topography, and physical obstructions.*
7. *The intensity and duration to which a toxic gas can incapacitate exposed individuals.*

Consequences can be described qualitatively, quantitatively, or both, with both receiving treatment relative to risk in the next chapter. Keep in mind that potential consequences can be significantly impacted (in a positive sense) through emergency planning and response actions. For example, well-executed evacuation procedures can sometimes prevent a significant number of injuries or deaths. Refer to Chapter 6 for more details on this subject.

Illustrative Example 15.4

A cup of instant coffee was recently placed in the microwave to heat it up to bring the water to a boil. Discuss the possible consequences associated with this “event.”

Solution

The individual heating the water runs the risk of the water in the cup “blowing up” into his or her face. Why? Water (alone) should never be heated in a microwave oven. If water is heated in this manner, something of a solid nature, for example, a wooden spoon, should be placed in the cup to diffuse the energy. It is, however, a much safer choice to boil the water in a tea kettle.

The “blowing up” problem arises because of a phenomenon known as superheating. It can occur anytime water is heated and will particularly

occur if the vessel in which the water is heated is new. What happens is that the water heats faster than the vapor bubbles can form. If the cup is very new, then it is unlikely to have small surface scratches inside it that provide a place for the bubbles to form. As the bubbles cannot form in the body of the water and release some of the heat that has built up, the liquid does not boil, and the liquid continues to heat up well past its boiling point. What then usually happens is that the liquid is bumped or jarred, which is just enough of a shock to cause the bubbles to rapidly form and expel the hot liquid. The rapid formation of bubbles is also why a carbonated beverage spews when opened after having been shaken.

Illustrative Example 15.5

Describe the difference(s) in consequence(s) between a toxic gas release and a fire/explosion.

Solution

The toxic gas release can lead to injuries and fatalities due to the toxicant's health effects on those exposed to it. The fire/explosion can lead to injuries and fatalities due to toxic effects of the flammable gas before it ignites or explodes but can also cause injuries and fatalities due to the thermal impact of the fire, the pressure wave of the explosion, as well as blunt trauma injuries and fatalities due to flying debris.

Illustrative Example 15.6

Discuss some of the consequence associated with a hydrogen sulfide (H_2S) leak from a tank.

Solution

H_2S is highly toxic. The following are some possible effects of a leak of H_2S gas.

1. Exposure to high concentrations (greater than 1000 ppmv) of H_2S can be lethal to humans in as little as 5 min.
2. Moderate concentrations (between 250 and 500 ppmv) may cause unconsciousness and respiratory paralysis.
3. In addition to its toxicity, H_2S is also an eye irritant. Low concentrations (as low as 20–30 ppmv) may cause conjunctivitis.
4. H_2S is a flammable gas that may form explosive mixtures with air and is capable of autoignition at temperatures above 260°C (500°F).
5. H_2S reacts violently with soda lime and many metal oxides resulting in incandescence in air and possibly progressing on to an explosion.

Illustrative Example 15.7

List four safeguards that can be used to protect against mechanical hazards.

Solution

1. Use personal protective equipment (PPE); wear rubber insulated gloves to handle electrical equipment. One may also need insulated clothing, such as rubber-soled shoes or boots—especially if the location is wet. One should check with a supervisor about what PPE is needed for a specific job. Never wear metal jewelry that could turn into a conductor.
2. Turn off power to electrical equipment before tests and repairs; then lock and tag it out, so it does not turn on by accident. Follow the equipment supplier's lockout/tagout procedures.
3. Inspect tools regularly. If a tool causes shocks, smokes, smells, or sparks, do not use it.
4. Keep some distance from power lines, and notify the power company before working near power lines. Never work closer than 10 ft on a ladder near power lines. Use insulated equipment (nothing metal). Never touch fallen power lines.

It is fair to state that the *consequence estimation* characterizes the effects resulting from a specific hazard/event and the impact of these effects on individuals, the environment, and property. The consequence models employed to estimate these effects fall into four major categories:

1. *Source models* that describe the release rate of chemicals from the process/equipment into the environment, including the rate of release of spilled vapors and volatile liquids into the atmosphere.
2. *Atmospheric dispersion models* that describe the transport and dispersion of the released chemicals into the atmosphere.
3. *Fire and explosion models* that describe the magnitude and physical effects resulting from a fire, explosion, or both.
4. *Effect models* that describe the impact of the effects of a fire, explosion, toxic gas, or hazardous chemical release on individuals, the environment, or property based on the three previous models.

Other models may be used to consider a host of other effects.

An example of an application of one of these consequence models is the atmospheric dispersion “puff” model discussed earlier in Chapter 10. A rather significant amount of data and information are available for sources that emit continuously to the atmosphere. Unfortunately, less is available on instantaneous or “puff” sources. Cases of instantaneous releases, as from an explosion, or short-term releases on the order of seconds, are also often of practical concern. An equation that may be used for estimates of ground level ($z=0$) concentration downwind from an instantaneous release from height, H^* , presented earlier in Equation 10.37, is

$$\begin{aligned}
 c(x, y, 0; H^*) = & \left[\frac{2 \dot{m}_T}{(2\pi)^{1.5} \sigma_x \sigma_y \sigma_z} \right] \exp \left[-\frac{1}{2} \left(\frac{x - ut}{\sigma_x} \right)^2 \right] \\
 & \times \exp \left[-\frac{1}{2} \left(\frac{H^*}{\sigma_z} \right)^2 \right] \exp \left[-\frac{1}{2} \left(\frac{y}{\sigma_y} \right)^2 \right] \quad (15.4)
 \end{aligned}$$

where

\dot{m}_T is the total mass of the release, g

u is the wind speed, m/s

t is the time after the release, s

x is the distance in the x direction to the center of the puff, m

y is the distance in the y direction from the centerline of the puff trajectory, m

$\sigma_x, \sigma_y, \sigma_z$ are dispersion coefficients in the x, y , and z direction (see also Chapter 10), respectively, m

Illustrative Example 15.8

A 20m high tank in a plant containing a toxic gas suddenly explodes. The explosion causes an emission of 400g/s for 3 min. A school is located 400m west and 50m south of the plant. If the wind velocity is 3.5m/s from the east, how many seconds after the explosion will the concentration reach a maximum in the school?

Solution

It should be noted that the maximum concentration in a puff is located at its center. Equation 15.4 is used to model the concentration of the center of the puff at locations downwind from the release. The movement of the center of the puff is assumed to travel at the speed of the wind during the release. Therefore, the time at which the maximum concentration will occur at the school is:

Time of travel of the center of the puff,

$$t = \frac{\text{Downwind distance in } x \text{ direction}}{\text{Wind speed}}$$

$$t = \frac{400 \text{ m}}{3.5 \text{ m/s}} = 114 \text{ s} \approx 2 \text{ min}$$

Illustrative Example 15.9

A 40m elevated vapor transfer line in a petroleum refinery suddenly ruptures. It is estimated that 375g/s of a hazardous gas is being emitted. If the emission from the rupture is brought under control 2 min later, estimate the concentration 1000m downwind and 100m displaced from the centerline 5 min later. The wind velocity is 4.0m/s and the Stability Category is D.

Solution

For this problem, $x = 1000 \text{ m}$, $y = 100 \text{ m}$, $H = 40 \text{ m}$, $u = 4 \text{ m/s}$

$$\dot{m}_T = (375 \text{ g/s})(2 \text{ min})(60 \text{ s/min}) = 45,000 \text{ g}$$

$$t = (5 \text{ min})(60 \text{ s/min}) = 300 \text{ s}$$

Since Stability Class D is applicable, the following dispersion coefficient values are obtained from Figures 10.2 and 10.3 and Table 10.3: $\sigma_x = 69 \text{ m}$, $\sigma_y = 69 \text{ m}$, $\sigma_z = 31.5 \text{ m}$.

Equation 15.4 applies since this emission is treated as an instantaneous point source. Substitution of values from the problem statement into Equation 15.4 yields the following:

$$\begin{aligned} c(x, y, 0; 40) &= \left[\frac{2(45,000 \text{ g})}{(2\pi)^{1.5}(69 \text{ m})(69 \text{ m})(31.5 \text{ m})} \right] \\ &\times \left\{ \exp \left[-\frac{1}{2} \left(\frac{1,000 \text{ m} - (4 \text{ m/s})(300 \text{ s})}{69 \text{ m}} \right)^2 \right] \right\} \\ &\times \left\{ \exp \left[-\frac{1}{2} \left(\frac{40 \text{ m}}{31.5 \text{ m}} \right)^2 \right] \right\} \left\{ \exp \left[-\frac{1}{2} \left(\frac{100 \text{ m}}{69 \text{ m}} \right)^2 \right] \right\} \end{aligned}$$

$$c(x, y, 0; 40) = (0.38 \text{ g/m}^3)(0.015)(0.447)(0.35) = 8.9 \times 10^{-5} \text{ g/m}^3$$

Illustrative Example 15.10

On January 2, 1988, a fuel oil tank at Ashland Oil terminal in Pennsylvania ruptured and a 35 ft high wave of 600,000 gal of Number 2 distillate fuel oil surged out over a containment dike into the Monongahela River. In this case, the containment dike was breached by the violence of the release of oil that surged over the dike. For this problem, assume a slightly different case in which a similar tank (containing 3.9 million gal of fuel) ruptures slowly, and a circular 5 ft high dike is designed to contain the entire contents of the tank.

1. If the radius of the dike is 192 ft, how far from the top of the dike will the level of the oil be?
2. Now assume that the worst foreseeable case will happen, i.e., record breaking rainfall for a long period following the release. The hazard in this case stems from the fact that the fuel is immiscible with water and has a lower density, so acts as a light nonaqueous phase liquid (LNAPL), floating on the surface of the water captured inside the dike. The heaviest daily rainfall recorded in this region of Pennsylvania over a recent 30 year

period is 5.68 in. Calculate how long it will take for the LNAPL to reach a “consequence condition,” that is, to become level with the top of the dike.

Solution

1. The depth of the fuel, h , held in the dike is calculated based on the volume of the spill divided by the cross-sectional area of the dike:

$$h = \frac{V}{A} = \frac{V}{\pi r^2} = (3.9 \times 10^6 \text{ gal}) \frac{(0.1337 \text{ ft}^3 / \text{gal})}{(\pi(192 \text{ ft}^2))} = 4.5 \text{ ft}$$

The oil will therefore rise to a level that is approximately 0.5 ft below the top of the dike.

2. The allowable depth of rainfall, H , within the dike before a “consequence” occurs is

$$H = 5.0 - 4.5 = 0.5 \text{ ft}$$

The time, t , that it will take for the LNAPL fuel to rise to the top of the dike is

$$t = \frac{H}{\text{Rainfall intensity}} = \frac{0.5 \text{ ft}}{[(5.68 \text{ in./day}) / (12 \text{ in./ft})]} = 1.06 \text{ day}$$

Because the water is denser than the oil, the oil will float on the surface and will rise to the top of the dike in approximately 1 day of the heavy rains assumed in the problem statement.

15.4 Failure Modes, Effects, and Criticality Analysis (FMECA)

Failure modes, effects, and criticality analysis (FMECA), also known as failure modes and effects analysis (FMEA), is a systematic, qualitative method by which equipment and system failures, and the resulting effects of these failures, are determined. FMECA is an inductive analysis, i.e., possible events are studied but not the reasons for their occurrences. FMECA investigates system/plant equipment with respect to their failure modes, the failure effect on the system/plant, and a criticality ranking for each failure. FMECA has some disadvantages: human error is not considered, and the approach concentrates on system components not the system linkages that often account for system failures. However, FMECA provides an easily updated, systematic reference listing of failure modes and effects that can be used in generating recommendations for equipment design improvements. Generally, this analysis is first performed on a qualitative basis; quantitative data can later

be applied to establish a criticality ranking that is often expressed as a probability of system failure.

Five steps are required for a thorough FMECA [6–11]:

1. The level of resolution of the study must be determined.
2. A format must be developed.
3. Problem and boundary conditions are then defined.
4. The FMECA table is completed.
5. The study results are reported.

The first step in FMECA is to determine a level of resolution for the study. If a system-level hazard is to be addressed, the equipment in the system must be studied; for a plant-level hazard, individual systems within the plant must be examined.

Once the level of resolution has been determined, a format must be developed—the one to be used consistently throughout the study. A minimum format should include each item or system analyzed, its description, failure modes, effects, and criticality ranking.

Defining the problem and boundary conditions includes identifying the plant or systems that are to be analyzed and establishing physical system boundaries. In addition, reference information on the equipment and its function within the system must be obtained. This can be found in piping and instrumentation design drawings as well as in the literature on individual components or equipment. The final step in the problem definition step is to provide a consistent criticality ranking definition. In a quantitative study, probabilities are often the method used for ranking. If the study is being conducted on a qualitative basis, relative scales are usually used as a ranking method. Table 15.3 summarizes the qualitative, relative scale hazard classes used in the aerospace industry [2]. If this type of scale is

TABLE 15.3

Suggested Criticality Rankings Based on Aerospace Hazard Classification

Criticality Ranking	Effects on System and Surroundings
I	Negligible effects
II	Marginal effects
III	Critical effects
IV	Catastrophic effects

Source: Adapted from U.S. EPA, *Technical Guidance for Hazard Analysis, Emergency Planning for Extremely Hazardous Substances*, EPA-OSWER-88-0001, Office of Solid Waste and Emergency Response, Washington, DC, 1987.

The final step in conducting an FMECA is to report the results. If the prepared table (i.e., Table 15.5) is complete, that may be sufficient. Often, however, a report of suggested design changes or alterations should also be included.

FMECA identifies single failure modes that either directly result in or contribute significantly to important accidents. As noted earlier, human/operator errors are generally not examined in an FMECA; however, the effects of an error in equipment operation are usually described by one of the equipment failure modes. It should also be noted that FMECA is not efficient for identifying combinations of equipment failures that lead to accidents.

Illustrative Example 15.11

List the key features (positive or negative) of FMEA.

Solution

An FMEA or FMECA has the following characteristics and key features:

1. It is particularly useful for analyzing possible equipment failures.
2. Logical information flow begins with a component failure and works to a final hazard event.
3. It is useful in reviewing existing or new facilities.
4. The analysis is limited in identifying likely operator errors.
5. The analysis is not effective for identifying logical sequence failures.

Overall, the FMECA is an effective method for looking at the effects that could result from the failure of a piece of equipment. This type of analysis focuses on the likely results or consequences of a component failure, such as a pump or a compressor, on other parts of the process, and hazards that may be introduced through this component and process failure.

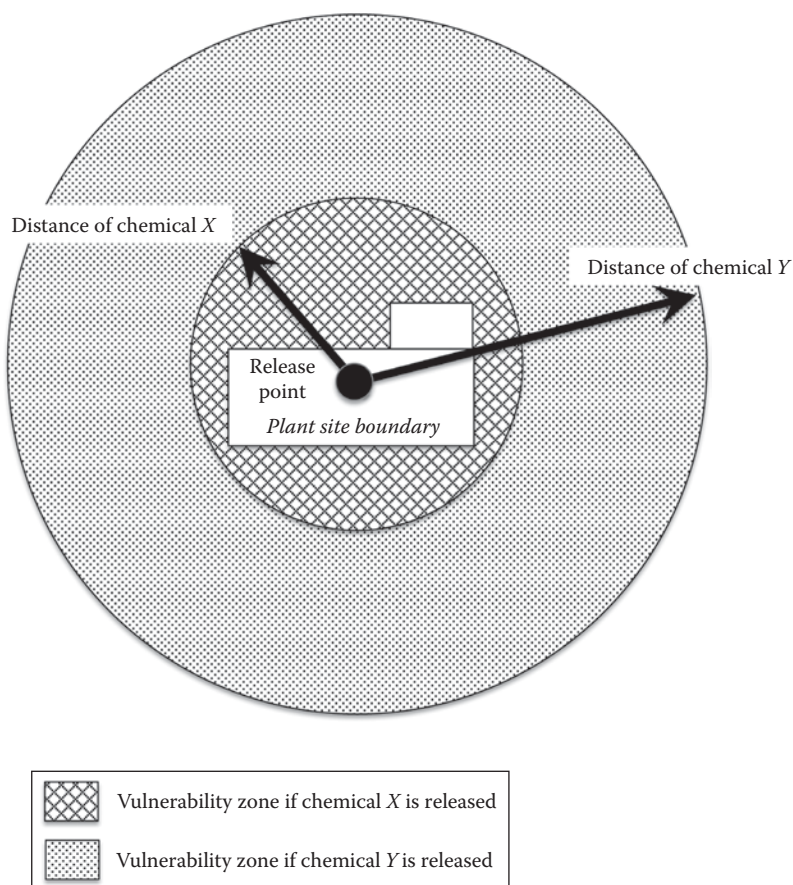
15.5 Vulnerability Analysis

Vulnerability analysis identifies areas in the community that may be affected or exposed; individuals in the community who may be subject to injury or death from certain specific hazardous materials; and what facilities, property, or environment may be susceptible to damage should a hazardous materials release occur. A comprehensive vulnerability analysis provides information on:

1. The extent of the vulnerable zones (i.e., an estimation of the area that may be affected in a significant way from a spill or release of a known quantity of a specific chemical under defined conditions)
2. The population, in terms of numbers, density, and types of individuals (e.g., facility employees; neighborhood residents; and people in hospitals, schools, nursing homes, prisons, day care centers, etc.) that could be within a vulnerable zone; the private and public property (e.g., critical facilities, homes, schools, hospitals, businesses, and offices) that may be damaged, including essential support services and facilities

The term vulnerability has been defined as “the susceptibility of life, property, and the environment to injury or damage if a hazard manifests its potential.” The vulnerability zone is generally that geographical area in which the concentration of an accidentally released substance may reach a critical concentration that may cause serious health effects. This critical concentration is often the *threshold limit value* (TLV), and details on calculation of these exposure concentrations are provided in Chapter 10. The area encompassed by this vulnerability zone depends on the amount of chemical released and the concentration of concern from a human health or environmental impact perspective. Figure 15.1 is a graphical representation of the vulnerability zones for a release of two different but extremely hazardous and/or toxic substances from a stationary facility. Figure 15.2 represents similar vulnerability zones for the same two pollutants involved in a transportation release. The vulnerability zone for a transportation scenario is represented as a corridor since the exact location of an accident may be difficult to predict. Once an accident has occurred, however, the actual vulnerability zone is assumed to be circular and similar to that for a chemical plant. The effect of different assumptions or the calculation of the radius of estimated vulnerability zones is provided in Figure 15.3. After estimating the vulnerability zone for a particular hazard, one should look for information in the following areas:

1. The number of people potentially exposed to this release at home, at work, or in recreational areas.
2. Places such as nursing homes, hospitals, and schools where more sensitive populations might be exposed.
3. Emergency service facilities within and near the zone, including communication facilities (e.g., local radio stations). Personnel in these facilities may not be available to respond to the emergency if the wind is blowing the hazard toward them.
4. Access and egress roads used for response, rescue, or evacuation. (Depending on wind direction, these roads may be unusable.)

**FIGURE 15.1**

Vulnerability zones for atmospheric releases of chemicals X and Y from a plant.

5. Other characteristics unique to the community that may cause significant problems, such as high traffic flow roads, methods for accident control, and diversion of traffic; communication centers in the potential path of a toxic/explosive vapor cloud; and recreational facilities such as sports or community centers.

Summarizing, a vulnerability analysis should provide comprehensive information on all the hazards deemed to be important following a hazard identification step.

Illustrative Example 15.12

Refer to Figure 15.3. Determine the consequences if an explosion occurs at the release site. Information for this potential accident is provided in Table 15.6.

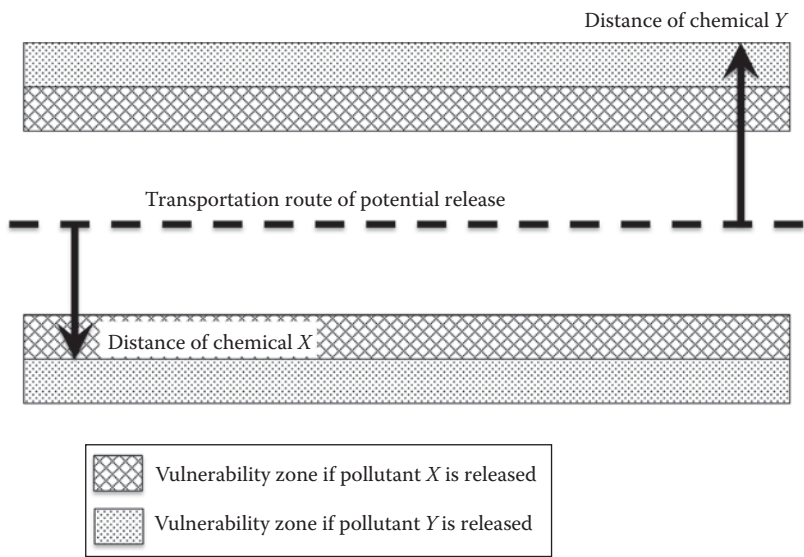


FIGURE 15.2
Vulnerability zones for transportation route with atmospheric releases of chemicals X and Y.

Solution

Consequence are listed in the following:

- Location A: 10 die
- Location B: $(10^2)(0.5) = 50$ die
- Location C: $(10^3)(0.25) = 250$ die
- Location D: $(10^4)(0.05) = 500$ die
- Location E: $(10^5)(0.01) = 1000$ die

$$\text{Total deaths} = \sum \text{Deaths at all locations} = 1810$$

The consequences of this explosion are that 1810 people will die in areas surrounding the release site.

Illustrative Example 15.13

The annual probability that an accidental radioactive release from a nuclear power plant will occur is 10^{-2} . Ricci Associates have estimated that:

1. 10% of the 10,000 people located within a mile of the plant will die
2. 1% of the 100,000 people located between 1 and 5 miles of plant will die
3. 0.001% of the 1,000,000 people located between 5 and 20 miles of the plant will die

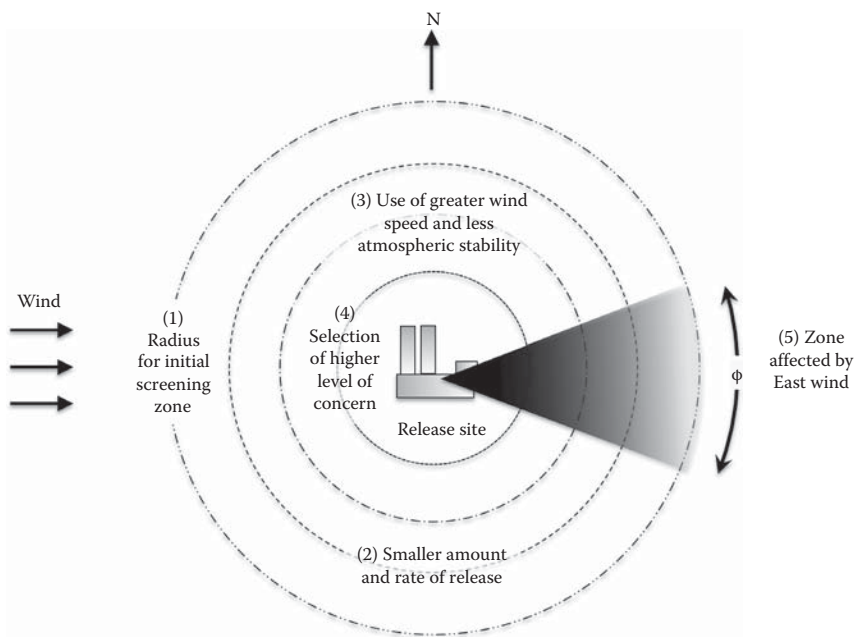


FIGURE 15.3
The effect of different assumptions on the calculation of the radius of estimated vulnerability zones and the effect of altering major assumptions on the downwind distance (radius) of the estimated vulnerability zone. Calculations made using the following: (1) credible worst-case assumptions for initial screening zone, (2) reevaluation and adjustment of quantity released and/or release rate of chemical, (3) reevaluation and adjustment of wind speed (increase) and air stability (decrease), (4) selection of a higher level of concern, and (5) affected zone of enclosed angle ϕ for East wind. Note that adjustment of two or more variables can have an additive effect on reducing the size of the estimated vulnerability zone. Note also that the relative sizes of the altered zones are not to scale (e.g., choosing a higher value for the level of concern does not always result in a smaller zone than the use of greater wind speed and less atmospheric stability).

TABLE 15.6
Consequence Table for Illustrative Example 15.12

Location Notation	Location (miles)	Number of People	Accident Effect
A	<1	10	All die
B	1–2	10 ²	50% die
C	2–3	10 ³	25% die
D	3–4	10 ⁴	5% die
E	>4	10 ⁵	1% die

No one outside the 20 miles range is affected. Calculate the consequences associated with an accidental release from the power plant.

Solution

A total of 1,110,000 people are potentially affected as follows:

$$(10^{-2})(10,000)(0.1) = (10^{-2})(1,000) = 10 \text{ will die of those located within 1 mile of the plant}$$
$$(10^{-2})(100,000)(0.01) = (10^{-2})(1,000) = 10 \text{ will die of those located between 1 and 5 miles of the plant}$$
$$(10^{-2})(1,000,000)(0.00001) = 0.1 \text{ will die of those located between 5 and 20 miles of the plant}$$

Thus, a total of $10 + 10 + 0.1 = 20.1 \approx 20$ people will die as a consequence of an accidental release of radioactivity from this power plant.

Illustrative Example 15.14

Translate the data and results of the previous illustrative example on to a figure similar to that provided in Figures 4.2 and 12.1.

Solution

See Figure 15.4.

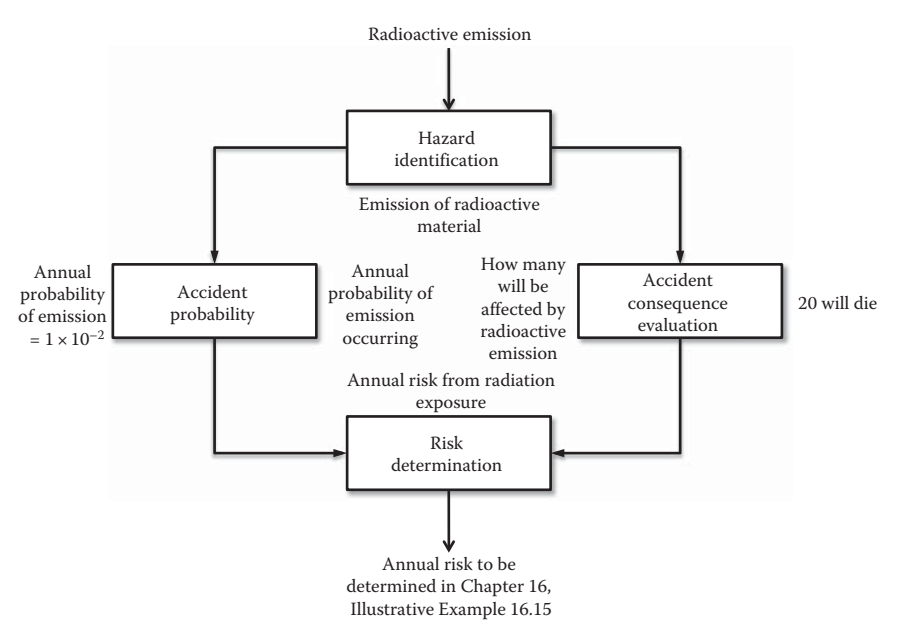


FIGURE 15.4 Nuclear power plant hazard risk assessment for Illustrative Problem 15.14.

Illustrative Example 15.15

Doyle and Doyle Associates (DADA) have been requested to conduct a HZRA at a chemical plant that is initially concerned with the consequences of an explosion resulting from the detonation of an unstable chemical. Based on an extensive literature search, the annual probability of the occurrence in any given year has been estimated by DADA to be 10^{-6} . The consequences in terms of the number of people killed/injured are estimated as follows:

1. All individuals within 100 m of the explosion center are killed.
2. All individuals between 100 and 200 m of the explosion center are severely injured.
3. All individuals outside a 200 m radius are unaffected.

Twenty people are located within 100 m of the explosion center and 25 are located beyond 200 m of the center; 100 individuals are located between 100 and 200 m of the explosion center. DADA have been specifically requested to calculate the consequences associated with the explosion.

Solution

Determine which individuals near the explosion center will be killed or injured if the accident occurs. As noted in the data provided:

1. A total of 20 individuals within a 100 m radius of the explosion center will die.
2. A total of 25 individuals in the 100–200 m range of the explosion center will be severely injured.
3. A total of 100 individuals will not be affected by the explosion.

Thus, the consequences of the potential exposure to the 145 individuals are:

$$\frac{20}{145} = 0.138 = 13.8\% \text{ will die}$$

and

$$\frac{25}{145} = 0.172 = 17.2\% \text{ will be severely injured}$$

and

$$\frac{100}{145} = \frac{0.690}{1.000} = \frac{69.0\%}{100\%} \text{ will not be affected}$$

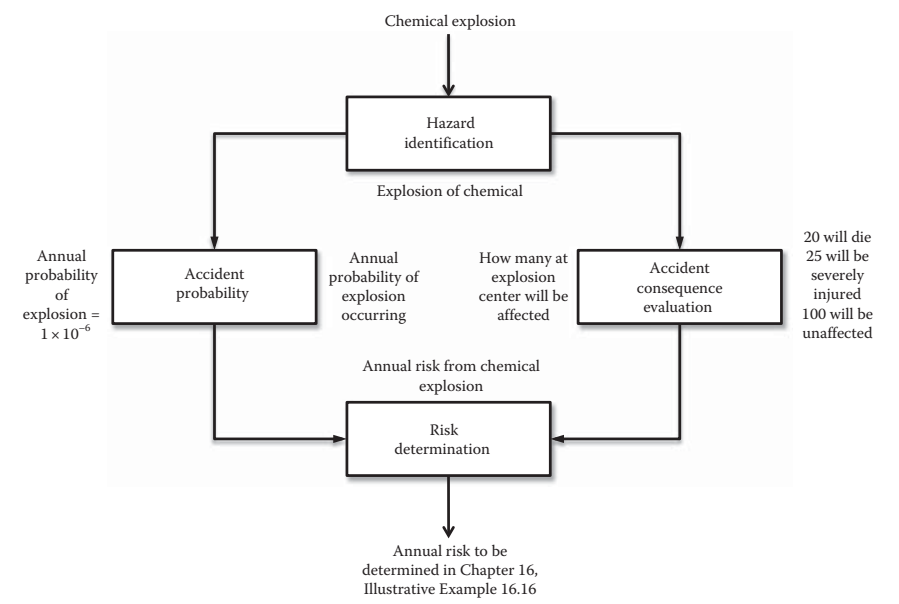


FIGURE 15.5
Chemical plant hazard risk assessment for Illustrative Example 15.16.

Illustrative Example 15.16

Transfer the data and results of the previous illustrative example into a figure similar to Figures 4.2 and 12.1.

Solution

The result is provided in Figure 15.5.

15.6 Event Tree Analysis

ETA is a technique for evaluating potential accident outcomes resulting from equipment failure or human error. ETA considers operator or safety system response to an initiating event in determining the potential accident outcomes. The results of the ETA are accident sequences, i.e., a chronological set of failures or errors that define an accident. These results describe the possible accident outcomes in terms of the sequence of events (successes or failures of safety functions) that follow an initiating event. The results are generally qualitative in nature. However, the results can be quantitative if the probabilities of all event sequences are available. ETA is well suited for processes that have safety systems or emergency procedures in place to

respond to specific initiating events, particularly in the chemical and nuclear industries [11].

An event tree model is started from the initial occurrence and built upon by sequencing the possible events and safety systems that come into play. The model displays, at a glance, branches of events that relate the proper functioning or failure of a safety device or system and the ultimate consequence of this proper function or failure. The model also allows quick identification of the various hazards that result from the single initial event.

The use of event trees is sometimes limiting for hazard analysis because it may lack the capability of quantifying the potential of the event actually occurring. The analysis may also be incomplete if all initial occurrences are not identified. Its use is beneficial in *examining*, rather than *evaluating*, the possibilities and consequences of a failure. For this reason, a fault tree analysis (FTA) may supplement an ETA to establish the probabilities of the event tree branches. Uncertainties and errors that arise are similar to those for an FTA, and it is important that information/data employed in the assessment should be fully documented to enable any subsequent checking and analysis.

Examples of event trees are provided in Figures 15.6 through 15.8. Figure 15.6 is concerned with an event tree in response to a power outage. Figure 15.7 is concerned with events occurring in response to a chemical

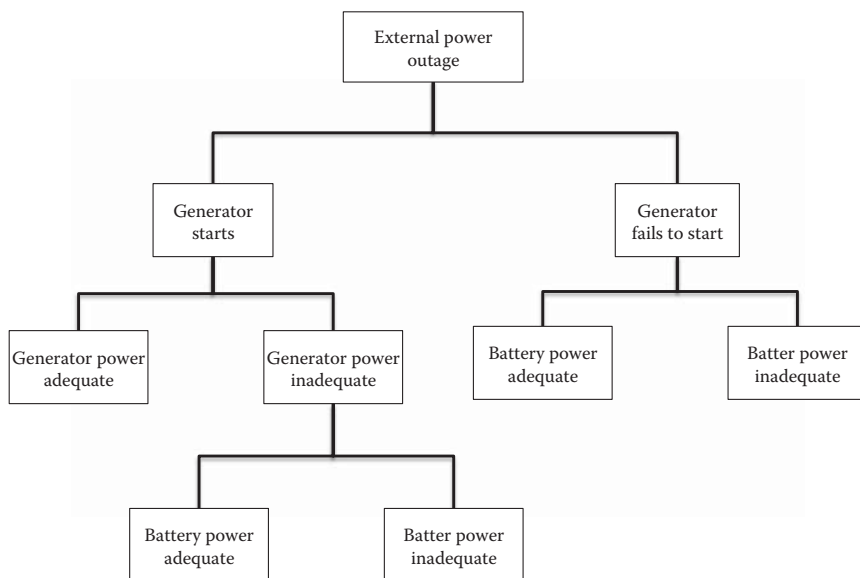


FIGURE 15.6

Event tree for a power outage.

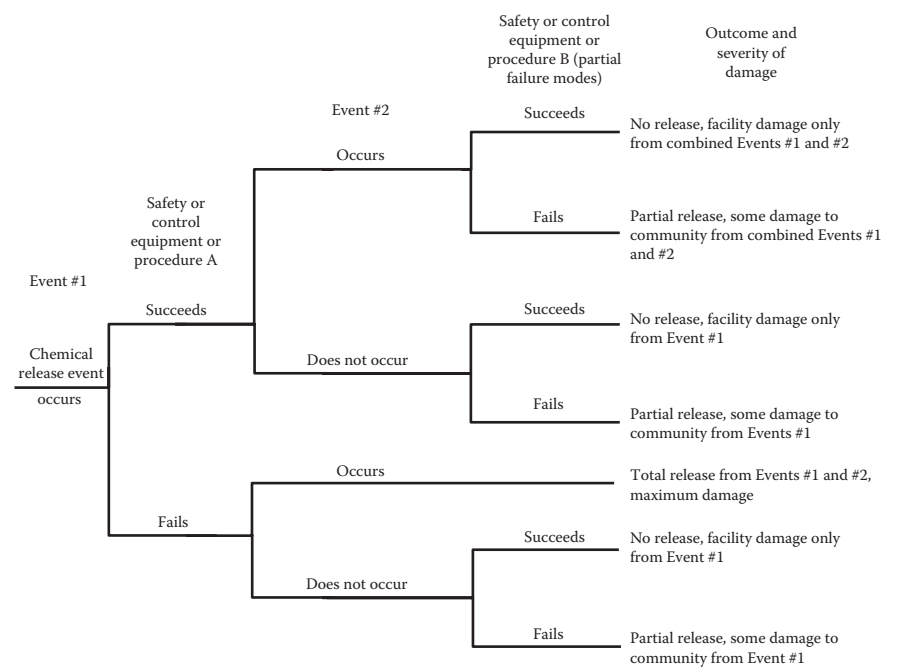


FIGURE 15.7
Event tree for a chemical release.

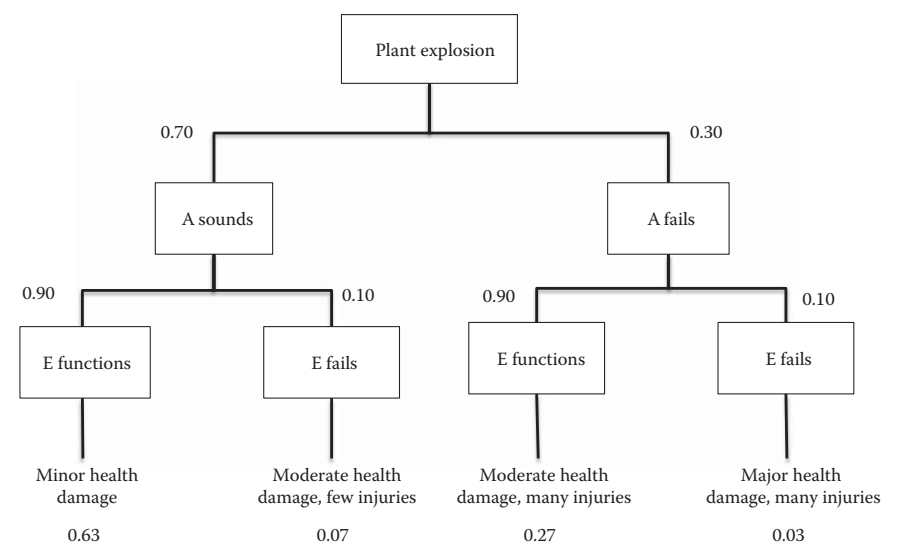


FIGURE 15.8
Event tree for plant explosion. A represents an alarm, E an exhaust system.

release, while Figure 15.8 provides some numerical data for a series of events occurring in response to a plant explosion [12,13].

In terms of staffing, a single analyst can perform an ETA, but normally a team of two to four people is preferred. The team approach promotes “brainstorming” that generally results in a well-defined event tree structure. The team should include at least one member with knowledge of ETA, with the remaining members having experience in the operations of the systems and knowledge of the chemical processes that are of interest in the analysis.

Summarizing, an event tree is a graphical logic model that both identifies and (often) quantifies possible outcomes from an initiating event. The event tree structure is therefore similar to that employed in FTAs; each event following the top or initiating event is based on the occurrence of a precursor event. Finally, the difference between an *event tree* and a *fault tree* should be noted. An ETA begins with a specific initiating event and works *forward* to evaluate potential accident outcomes. A FTA begins with the ultimate consequence and works *backward* to the possible causes and failures of this consequence. The analysis “direction” for either is top-down or left-right.

Illustrative Example 15.17

Describe the difference between the following:

1. Event
2. External event
3. Initiating event
4. Intermediate event
5. Primary event

Solution

These terms are described in Table 15.7.

Illustrative Example 15.18

Describe the difference between a vulnerability analysis and an ETA.

Solution

A vulnerability analysis identifies those regions that may be affected or exposed; individuals who may be subject to injury or death; and those facilities, property, or the environment that may be susceptible to damage should a hazardous materials release occur.

ETA is a technique for evaluating potential accident outcomes resulting from a specific initiating event. The results of the ETA are chronological sets of failures or errors that may be used to define an accident.

TABLE 15.7
Event Definitions

Type of Event	Description
Event	An occurrence involving equipment performance or human action or an occurrence external to the system that causes a system upset. In this chapter, an event is associated with an accident, either as the cause or a contributing cause of the accident, or as a response to the accident-initiating event
External event	An occurrence external to the system/plant, such as an earthquake or flood, or an interruption of utilities such as electric power or process air
Initiating event	An event that will result in an accident unless systems or operations intervene to prevent or mitigate the accident
Intermediate event	An event or an accident event sequence that helps to propagate the accident or helps to prevent the accident or mitigate the consequences
Primary event	A basic independent event for which its frequency can be obtained from experience or testing

Illustrative Example 15.19

Construct a decision tree given the following information:

- Date: a couple’s anniversary
- Decision: buy flowers or do not buy flowers
- Consequences (buy flowers): domestic bliss or suspicious wife
- Consequences (do not buy flowers): status quo, or wife in tears, or husband in doghouse

Solution

This is an event tree example. Begin by setting the initial event in “tree” format with this initial event being the top event (Figure 15.9). Set up the first branch from the initial event. This is the first decision point (Figure 15.10). Complete the tree. Note that the bottom four events evolve from what may be defined as resolution of uncertainty points (Figure 15.11).

As indicated earlier, in contrast to a fault tree, which works backward from a consequence to possible causes, an event tree works forward from the initiating (or top) event to all possible outcome consequences. Thus,



FIGURE 15.9
Top event for Illustrative Example 15.19.

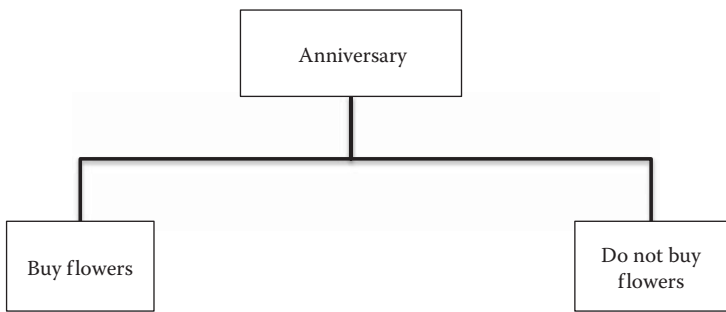


FIGURE 15.10
First decision point for Illustrative Example 15.19.

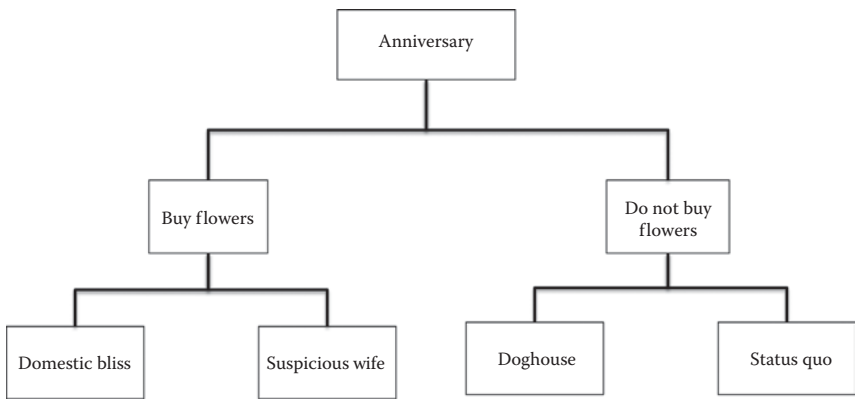


FIGURE 15.11
Final event tree application for Illustrative Example 15.19.

this type of tree provides a diagrammatic representation of sequences that begin with a so-called initiating event and terminate in one or more outcomes and resulting consequences. It primarily finds application in hazard analysis.

Illustrative Example 15.20

If a plant fire occurs, a smoke alarm sounds with a probability of 0.9. The sprinkler system functions with a probability of 0.7 whether or not the smoke alarm sounds. The resulting consequences of the sequence of outcomes are minor fire damage (alarm sounds and sprinkler works), moderate fire damage with few injuries (alarm fails and sprinkler works), moderate fire damage with many injuries, and major fire damage with many injuries (alarm fails and sprinkler fails). Construct an

event tree and indicate the probabilities for each of the four outcome consequences.

Solution

The first set of outcomes of the plant fire with their probabilities is shown in Figure 15.12. The second set of outcomes of the plant fire and their probabilities is shown in Figure 15.13. The final set of outcomes and the probabilities of the resulting consequences of minor fire damage, moderate fire damage with few injuries, moderate fire damage with many injuries, and major fire damage with many injuries are shown in Figure 15.14. Note that for each branch in an event tree, the sum of probabilities must equal 1.0.

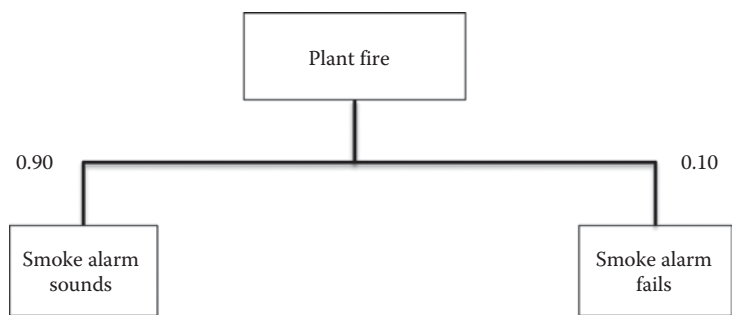


FIGURE 15.12
Event tree with first set of outcomes for Illustrative Example 15.20.

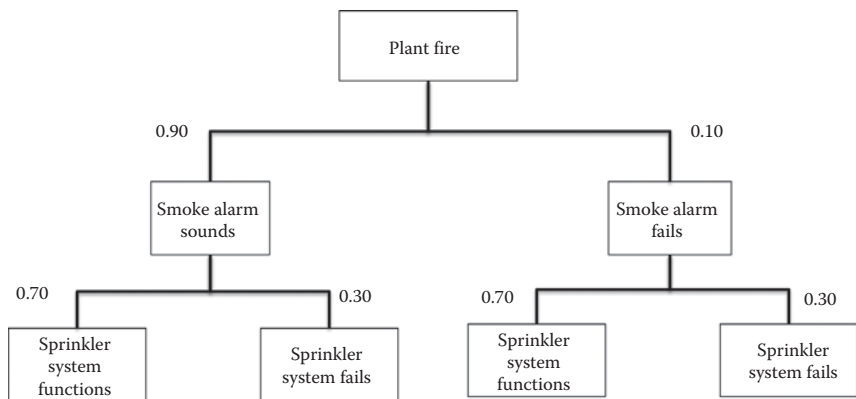
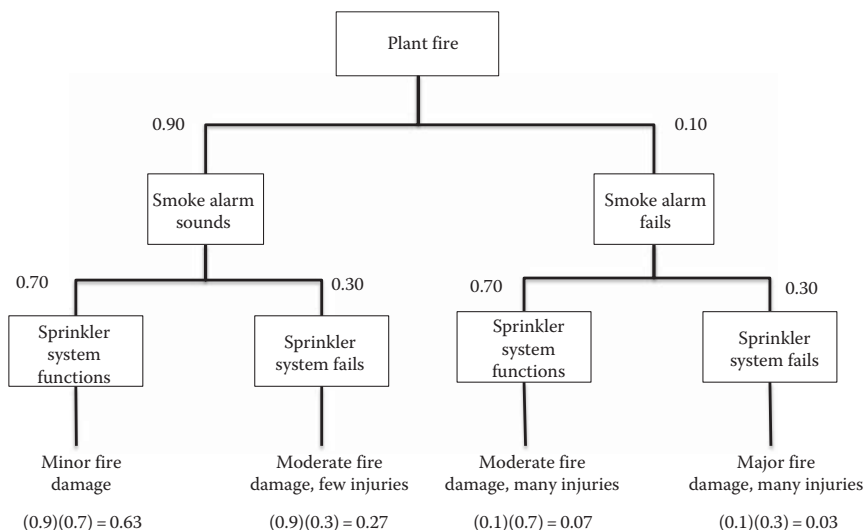


FIGURE 15.13
Event tree with second set of outcomes for Illustrative Example 15.20.

**FIGURE 15.14**

Event tree with final set of outcomes and resulting consequences for Illustrative Example 15.20.

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16

Hazard Risk Characterization

16.1 Introduction

This final chapter in Part III serves to introduce the general subject of hazard risk assessment and analysis, including cause–consequence risk evaluation. The cause–consequence aspect of this topic is perhaps the key to understanding hazard risk. As such, it is treated in a separate section later in this chapter.

As an example, hazard risk assessment can address the likelihood (probability) of an accidental release of a hazardous material and the actual consequences that might occur, based on the estimated vulnerable zones. The risk assessment is a judgment of the probability and severity of consequences based on the history of previous incidents, local experience, and the best available current technological information. It provides an estimation of:

1. The likelihood (probability) of an accidental release based on the history of current conditions and controls at a facility, consideration of any unusual environmental conditions (e.g., areas in flood plains), or the possibility of simultaneous emergency incidents (e.g., flooding or fire hazards resulting in the release of hazardous materials)
2. The severity of consequences of human injury that may occur (acute, delayed, and/or chronic health effects), the number of possible injuries and deaths, and the associated high-risk groups
3. The severity of consequences on critical facilities (e.g., hospitals, fire stations, police departments, and communication centers)
4. The severity of consequences of damage to property (temporary, repairable, and permanent)
5. The severity of consequences of damage to the environment

The risk assessment process also attempts to attach meaning to a risk that has been calculated, including such factors as economic, social, and technological, plus selecting a course of action concerning the risk. Finally,

interpreting and communicating the calculated risk value(s) to the public can be accomplished in a number of ways including the following:

1. Comparison with other known risks
2. Providing perspective on the frequency/occurrence(s) of the risk
3. Explaining the sensitivity of the risk results to changes in input model data and scenario assumptions

The risk management process generally involves selecting a course of action that best addresses the risk in question and can include the following:

1. A cost–benefit analysis of risk
2. Measuring public perception
3. Determining acceptable levels of risk

Following this introductory section, topics addressed in this chapter include:

1. Risk characterization
2. Public perception of risk
3. Risk communication
4. Cause–consequence analysis
5. Qualitative hazard risk assessment
6. Uncertainties/limitations
7. Quantitative hazard risk assessment

Illustrative Example 16.1

Why should risk assessment procedures be employed by society?

Solution

Because so many hazards exist in everyday life, risk assessment must be used as a tool for evaluating those that are the most pressing or most hazardous. Over time, one may find that some activities are more hazardous than once perceived (i.e., smoking cigarettes or manufacturing polychlorinated biphenyls [PCBs]). Once the evidence is evaluated, these practices may be either stopped or limited. An assessment on an unknown chemical hazard or potentially unsafe practice attempts to project what the consequences might be without waiting for final proof of an adverse impact.

Illustrative Example 16.2

List some actions that should be taken when attempting to reduce risks arising from a chemical release.

Solution

1. Eliminate the hazard.
2. Attempt to reduce the duration of the release.
3. Attempt to reduce the frequency of the release.
4. Attempt to reduce the cause for the release.
5. Reduce the consequences associated with any release.
6. Change the physical design, control system, or operating condition.
7. Change the process.
8. Change the process materials.
9. Reduce the quantity of material produced and stored.

Illustrative Example 16.3

List some of the types of information a risk assessment can provide.

Solution

1. Identification and description of hazards and accident events that could lead to undesirable consequences
2. A qualitative estimate of the likelihood and consequence of each accident event sequence
3. A relative ranking of the risk of each hazard and accident event sequence
4. Some suggested approaches to risk reduction

For the chemical process industry, these results are normally provided to plant management and engineering or research groups, as appropriate, so that overall plant and process safety can be improved, and both on- and offsite risks can be minimized.

Illustrative Example 16.4

Discuss the problems in valuing life relative to characterizing risk.

Solution

There are various estimates of the value of life, ranging at the high end from about \$2 million per life to about \$200,000 per life. The choice of value in this range depends a great deal on the ethical basis upon which the estimates are made. Beyond being seemingly callous in putting a “price tag” on a person’s life, the decision to value one life more than another subjects the risk assessment to potential criticism of racism, bias, insensitivity, subjectivity, etc. When attempting to develop a cost–benefit analysis involving risk of human fatalities, it is essential that life valuation be done as objectively as possible, and with as much public input and involvement as is reasonably possible to ensure that the process is unbiased, fair, and equitable.

16.2 Risk Characterization

Risk characterization estimates the risk associated with a process under investigation. The result of this characterization is a number that represents the probability of adverse effects from that process and/or from a substance released from that process. For instance, a risk characterization for all effects from a nuclear power plant might be expressed as one additional cancer case per 1 million people.

Once a risk characterization is made, the meaning of that risk must be evaluated. Public environmental and health agencies generally only consider risk greater than 10 in 1 million (1×10^{-5} or 10×10^{-6}) to be significant risks warranting action.

The major types of risk include (see also Chapter 1) the following:

1. *Individual risk*: This provides a measure of the risk to a person in the vicinity of a hazard/accident, including the nature of the injury or other undesired outcomes, and the likelihood of its occurrence. Individual risk is generally expressed in terms of a likelihood or probability of a specified undesired outcome per unit of time. For example, the individual risk of a fatality at a particular location near a nuclear power plant might be expressed as 1 in 100,000 per year or 10^{-5} per year. The risk to a person at a particular location depends on the probability of occurrence of the hazard event and on the probability of an adverse impact at that location should the event occur.
2. *Maximum individual risk (MIR)*: This is the maximum risk to an individual. This individual is considered to have a 70 year lifetime of exposure to a process or a chemical. For a discharge from a stack, for instance, the individual is considered to live downwind of the stack, never leaving this spot for every hour and every day of a 70 year life span. The MIR is the risk to an individual subjected to this worst case, lifetime exposure to this hazard.
3. *Population risk (PR)*: This is the risk to a population as a whole, expressed as a given number of deaths per thousand or per million people potentially exposed to the hazard.
4. *Societal risk*: This represents a measure of the risk to a group of people, including the risk of incidents potentially affecting more than one person. Individual risk is generally not significantly affected by the number of people involved in an incident.
5. *Risk indices*: A risk index is a single-number measure of the risk associated with a facility. Some risk indices are qualitative or semiquantitative, ranking risks in various general categories. Risk indices may also be quantitative averages or benchmarks based on other risk measures.

TABLE 16.1
Presentation of Measures of Risk

Risk Measure	Presentation Format
Equivalent social cost index	A single-number index value representation
Fatal Accident Rate (FAR)	A point estimate of fatalities/10 ⁸ exposure hours
Individual hazard index	An estimate of peak individual FAR
Average rate of death	A number representing the estimated average number of fatalities per unit time
Mortality index	A single-value representation of consequence

Other general indices are provided in Table 16.1.

The reader should note that the risk to people can be defined in terms of either injury or fatality. The use of injuries as a basis of risk evaluation may be less disturbing than the use of fatalities. However, this introduces problems associated with defining the degree of injury and comparability between different types of injuries when trying to make relative risk comparisons. Further complications can arise in a risk assessment when dealing with multiple hazards. For example, how are second-degree burns, fragment injuries, and injuries due to toxic gas exposure combined? Even where only one type of effect (e.g., threshold toxic exposure) is being evaluated, different durations of exposure can markedly affect the severity of the injury sustained by the exposed individuals.

Illustrative Example 16.5

Can a risk characterization provide information on exactly what to do about a specific hazard?

Solution

No. Risk characterization is often imprecise in that it draws upon available information about a hazard, applies scientific principles, and then provides guidance on potential risk. Risk characterization helps identify hazards. How that information is used to decide what steps, if any, to take to reduce the hazard is not part of the risk characterization process.

Illustrative Example 16.6

Compare individual hazard risk with population risk.

Solution

Individual hazard risk is that risk borne by individual persons within a population. When doing a risk assessment, individual risks are frequently calculated for some or all of the individuals in the population being studied and are then put into the context of where they fall in the

distribution of risks for the entire population. Population risk refers to an estimate of the extent of harm for a complete population or for a segment of a population. In theory, an estimate of the extent of the effects a population might incur can be calculated by summing the individual risks for all individuals within the population or the population segment of interest.

16.3 Public Perception of Risk

In making an effort to understand the significance of risk analyses, it is helpful to place the estimated risks in the same perspective as other everyday risks that have been determined by a similar methodology. Table 16.2 lists a number of risks for comparison. These were derived from actual statistics and reasonable estimates [1,2]. People often overestimate the frequency and seriousness of dramatic, sensational, dreaded, well-publicized causes of death, and underestimate the risks from more familiar, accepted causes that relentlessly claim lives one by one. Indeed, risk estimates by “experts” and laypeople (or “the public”) differ significantly on many key environmental issues. This disconnect between the public and risk experts, and the reasons for it are extremely important because the public generally does not trust experts to make important risk decisions for them.

To make wise judgments requires that individuals know what experts’ estimates of the risks are, what it would cost (in terms of their other values) to reduce them, and how certain and free of bias the estimates are. Scientific precision is not needed, but a sense of whether a risk is “big,” “medium,” “small,” or “infinitesimal” is. The challenge to risk experts is to provide this information in ways so that it can be properly incorporated in the view of people who have little time or patience for arcane scientific discourse. Success in communicating and managing risk should not be measured by whether the public chooses the set of outcomes that minimizes risk as estimated by the experts; but instead when those outcomes are knowingly chosen by a well-informed public. This topic of risk communication is treated next.

16.4 Risk Communication

Environmental and hazard risk communication is one of the more important problems that industry faces. Since the mid-1980s, public concerns about the environment have grown faster than concerns about virtually any other national problem [3], except perhaps terrorism.

TABLE 16.2

Lifetime Risks of Fatality Faced by Individuals

Cause of Risk	Lifetime (70 Year) Risk of Death, per Million Individuals
Cigarette smoking	252,000
All cancers	196,000
Construction sector employment	42,700
Agriculture sector employment	42,000
Police killed in line of duty	15,400
Air pollution (Eastern United States)	14,000
Motor vehicle accidents (traveling)	14,000
Home accidents	7,700
Frequent airplane travel	3,500
Pedestrian hit by a motor vehicle	2,900
Alcohol, light drinker	1,400
Background radiation at sea level	1,400
Peanut butter, four tablespoons per day	560
Electrocution	370
Tornado	42
Drinking water containing chloroform at the maximum allowable EPA limit	42
Lightning strike	35
Living 70 years in a zone of maximum impact from modern municipal airports	1
Smoking 1.4 cigarettes	1
Drinking 0.5L of wine	1
Traveling 10 miles by bicycle	1
Traveling 30 miles by car	1
Traveling 1000 miles by jet plane (air crash)	1
Traveling 6000 miles by jet plane (cosmic rays)	1
Drinking water containing trichloroethylene at the maximum allowable EPA limit	0.1

There are two major categories of risk: nonfixable and fixable. Nonfixable risks can never substantially be reduced, such as cancer-causing sunlight or cosmic radiation. Fixable risks can be reduced, and include those risks that are both large and small. There are so many of these fixable risks that all of them can never be successfully managed, and choices and priorities must be made on where to begin. When it comes to risk reduction, the outcome should be to produce the most reduction possible for the least expenditure of time and resources, taking into account that people fear some risks more than others. This essentially, and often, means that the technical community should concentrate on the big fixable targets and leave the smaller ones to later.

Risk communication comes into play because citizens ultimately determine which risks government agencies attack first. On the surface, it appears practical to remedy the most severe risks first, leaving the others until later, or perhaps, if the risks are small enough, never remedying the others at all. However, the behavior of individuals in everyday life often does not conform to this view.

Two earlier environmental issues that dramatized the need for intelligent and proper risk communication were:

1. Gasoline that contains lead
2. Ocean incineration

Although specific details of these issues are beyond the scope of this chapter, information on both topics is provided in Ref. [4].

There are no easy prescriptions for successful risk communication. However, those who have studied and participated in recent debates about risk generally agree on seven cardinal rules. These personalized rules apply equally well to the public and private sectors. Although many of these rules may seem obvious, they are continually and consistently violated in practice. Thus, a useful way to consider these rules is to focus on why they are frequently not followed [5].

1. *Accept and involve the public as a legitimate partner.* A basic tenet of risk communication in democracy is that people and communities have a right to participate in decisions that affect their lives, their property, and the things they value.

Guidelines: Demonstrate respect for the public and underscore the sincerity of effort involving the community early, before important decisions are made. Involve all parties that have an interest or stake in the issue under consideration. If you are a government employee, remember that you work for the public. If you do not work for the government, the public still holds you accountable.

Point to consider: The goal in risk communication in a democracy should be to produce an informed public that is involved, interested, reasonable, thoughtful, solution oriented, and collaborative. It should not be to diffuse public concerns or replace action.

2. *Plan carefully and evaluate your efforts.* Risk communication will be successful only if carefully planned.

Guidelines: Begin with clear, explicit risk communication objectives, such as providing information to the public, motivating individuals to act, stimulating response to emergencies, and contributing to the resolution of conflict. Evaluate the information you have about the risks and know its strengths and weaknesses. Classify and segment

the various groups in the audience. Aim communications at specific subgroups in the audience. Recruit spokespeople who are good at presentation and interaction. Train staff, including technical staff, in communication skills; reward outstanding performance. Whenever possible, pretest your messages. Carefully evaluate your efforts and learn from your mistakes.

Point to consider: There is no such entity as “the public”; instead, there are many publics, each with their own interests, needs, concerns, priorities, preferences, and organizations. Different risk communication goals, audiences, and media require different risk communication strategies.

3. *Listen to the public’s specific concerns.* If you do not listen to the people, you cannot expect them to listen to you. Communication is a two-way activity.

Guidelines: Do not make assumptions about what people know, think, or want done about risks. Take the time to find out what people are thinking. Use techniques such as interviews, focus groups, and surveys. Let all parties that have an interest or stake in the issue be heard. Identify with your audience and try to put yourself in their place. Recognize people’s emotions. Let people know that you understand what they said, addressing their concerns as well as yours. Recognize the “hidden agendas,” symbolic meanings, and broader economic or political considerations that often underlie and complicate the task of risk communication.

Point to consider: People in the community are often more concerned about such issues as trust, credibility, competence, control, voluntariness, fairness, caring, and compassion than about mortality statistics and the details of a quantitative risk assessment.

4. *Be honest, frank, and open.* In communicating risk information, trust and credibility are your most precious assets.

Guidelines: State your credentials; but do not ask or expect to be trusted by the public. If you do not know an answer or are uncertain, say so. Get back to people with answers. Admit mistakes. Disclose risk information as soon as possible (emphasizing any reservations about reliability). Do not minimize or exaggerate the level of risk. Speculate only with great caution. If in doubt, lean toward sharing more information, not less, or people may think you are hiding something. Discuss data uncertainties, strengths, and weaknesses, including the ones identified by other credible sources. Identify worst-case estimates as such and cite ranges of a risk estimate when appropriate.

Point to consider: Trust and credibility are difficult to obtain. Once lost, they are almost impossible to regain completely.

5. *Coordinate and collaborate with other credible sources.* Allies can be effective in helping you communicate risk information.

Guidelines: Take time to coordinate all interorganizational and intraorganizational communications. Devote effort and resources to the slow, hard work of building bridges with other organizations. Use credible and authoritative intermediates. Consult with others to determine who is best able to answer questions about risk. Try to issue communications jointly with other trustworthy sources (e.g., credible university scientists and/or professors, physicians, or trusted local officials).

Point to consider: Few things make risk communication more difficult than conflicts or public disagreements with other credible sources.

6. *Meet the needs of the media.* The media are a prime transmitter of information on risks; they play a critical role in setting agendas and in determining outcomes.

Guidelines: Be open and accessible to reporters. Respect their deadlines. Provide risk information tailored to the needs of each type of media (e.g., graphics and other visual aids for television). Prepare in advance and provide background material on complex risk issues. Do not hesitate to follow up on stories with praise or criticisms, as warranted. Try to establish long-term relationships of trust with specific editors and reporters.

Point to consider: The media are frequently more interested in politics than in risk; more interested in simplicity than in complexity; and more interested in danger than in safety.

7. *Speak clearly and with compassion.* Technical language and jargon is useful as professional shorthand but is a barrier to successful communication with the public.

Guidelines: Use simple, nontechnical language. Be sensitive to local norms, such as speech and dress. Use vivid, concrete images that communicate on a personal level. Use examples and anecdotes that make technical risk data come alive. Avoid distant, abstract, unfeeling language about deaths, injuries, and illnesses. Acknowledge and respond (both in words and with action) to emotions that people express, which can include anxiety, fear, anger, outrage, and helplessness. Acknowledge and respond to the distinctions that the public views as important in evaluating risks, e.g., voluntariness, controllability, familiarity, dread, origin (natural or man made), benefits, fairness, and catastrophic potential. Use risk comparisons to help put risks in perspective but avoid comparisons that ignore distinctions which people consider important. Always try to include a discussion of actions that are under way or can be taken. Tell people

what you cannot do. Promise only what you can do and be sure to do what you promise.

Point to consider: Regardless of how well you communicate risk information, some people will not be satisfied. Never let your efforts to inform people about risks prevent you from acknowledging and saying that any illness, injury, or death is a tragedy. And finally, if people are sufficiently motivated, they are quite capable of understanding complex risk information, even if they may not agree with you.

16.5 Cause–Consequence Analysis

Cause–consequence risk evaluation combines the earlier discussed fault tree (Chapter 14) and event tree (Chapter 15) analyses to relate specific accident consequences to causes [6]. The process of this cause–consequence evaluation usually proceeds as follows:

1. Select an event to be evaluated.
2. Describe the safety system(s)/procedure(s)/factor(s) that would interrupt the path of the accident.
3. Perform a fault tree analysis to determine the event or function that failed.
4. Perform an event tree analysis to find the path(s) an accident may follow.
5. Rank the results qualitatively on the basis of severity of consequences or perhaps quantitative calculations.

Cause–consequence analysis attempts to characterize the (physical) effects resulting from an accident/event and the impact of these (physical) effects on individuals, the environment, and property. It can identify the basic cause of accident and accident consequences, with the combined results yielding information required in a risk assessment study. Causes and consequence received treatment in Chapters 14 and 15, respectively, and the combined analysis of the two provides information regarding overall accident risk.

A major strength of cause–consequence analysis is its use as a communication tool. For example, a cause–consequence diagram displays the interrelationships between the accident outcomes (consequences) and their basic causes. The method can be used to quantify the expected frequency of occurrence of the consequences if the appropriate data are available.

Some consequence models and/or equations (see Chapter 15) used to estimate the potential for damage or injury or death can be characterized as follows [7]:

1. *Source models* describe the release rate of material from process equipment into the environment and the rate of release of spilled vapors and volatile liquids into the atmosphere.
2. *Dispersion models* describe the behavior of the released material in the atmosphere as it is transported in a vapor or fine droplet state by advection via the wind.
3. *Fire and explosion models* describe the magnitude and physical effects (heat radiation, explosion overpressure) resulting from a fire or explosion.
4. *Effect models* describe the impact of the physical effects of a fire, explosion, or toxic gas release on exposed people, the environment, or property, based on inputs from the source, dispersion, and fire and explosion models.

Other models may be used to consider the effects of escape or evacuation, sheltering, protective equipment, or other factors (e.g., water contamination) that may be considered in a risk study.

Likelihood estimation, sometimes called *frequency estimation*, characterizes the probability of occurrence for each potential incident considered in the analysis. The major tools used for likelihood estimation are listed below [8]:

1. *Historical data* are used for facility types where there is an extensive historical record available from similar or identical installations.
2. *Failure sequence modeling techniques* such as fault tree analysis are used to estimate the likelihood of incidents in facilities where historical data are unavailable or are inadequate to accurately estimate the likelihood of the hazard incidents of concern. Other modeling techniques may be required to consider the impact of external events (earthquakes, floods, etc.), common cause failures, human factors, and human reliability.
3. *Expert judgment* quantifies an expert's state of knowledge or perceptions of the likelihood of an incident. This knowledge may be based on historical data, insights gained from models, experience, or a combination of these factors. See also the discussion of the Delphi panel approach in Chapters 1 and 11.

Illustrative Example 16.7

Discuss staffing and cost requirements for a cost-consequence analysis.

Solution

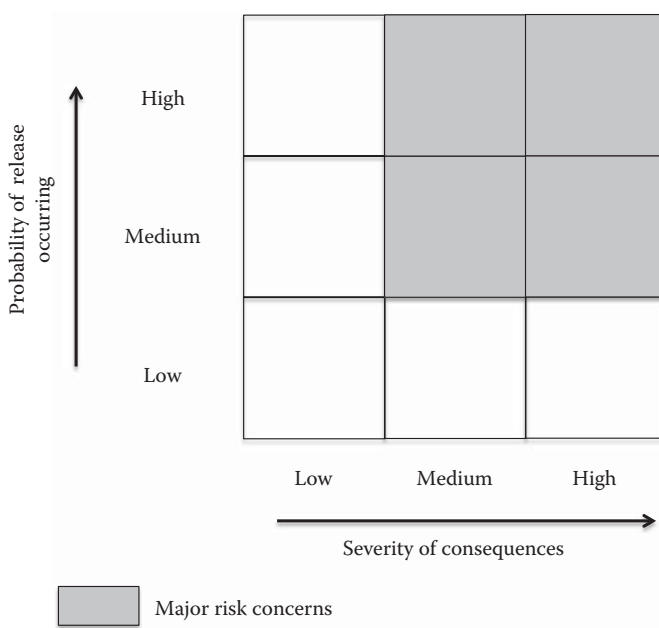
Staffing and cost requirements are as follows: cause–consequence analysis is best performed by a small team (two to four people) with a variety of expertise. One team member should be experienced in cause–consequence analysis (or fault tree and event tree analysis), with the remaining members having experience in the operations and interactions of the systems included in the analysis. Time and cost requirements for cause–consequence analysis are highly dependent on the number, complexity, and level of resolution of the events included in the analysis. Scoping-type analyses for several initiating events can usually be accomplished in a week or less. Detailed cause–consequence analyses may require 2–6 weeks, depending on the complexity of any supporting fault tree analyses that are required.

16.6 Qualitative Hazard Risk Assessment

As with health risk, hazard risk information can be presented either qualitatively or quantitatively. This section provides a description of qualitative risk procedures relevant for hazard risk characterization.

As described in the previous chapter, consequences of accidents can be classified qualitatively by their degree of severity. General factors that help to determine the degree of severity for chemical releases are the concentration at which the hazard is released, the duration of the release that governs the total quantity of the chemical released, the length of time that a person within the environment is exposed to the hazard based on the duration of the release and their ability to take avoidance action, and the overall toxicity of the hazard. The worst-case consequence or scenario is defined as a conservatively high estimate of the most severe accident identified. On this basis, one can rank the consequences of accidents into low, medium, and high degrees of severity. A low degree of severity means that the hazard is nearly negligible, and the injury to person, property, or the environment may be observed only after an extended period of exposure. The degree of severity or risk is considered to be medium when the accident is serious but not catastrophic, the toxicity of the chemical released is significant, or the concentration of a less toxic chemical is large enough to cause injury or death to individuals and damage to the environment unless immediate action is taken. There is a high degree of risk when the accident is catastrophic or the concentration and toxicity of a hazard are large enough to cause injury or death to many individuals quickly, and there is long-term damage to the surrounding environment.

Figure 16.1 provides a graphical, qualitative representation of the risk associated with both the probability of occurrence and consequences of a chemical release [9]. In line with the discussion above, one might assign the

**FIGURE 16.1**

Qualitative probability consequence risk analysis.

following definitions regarding the *probability* of a hazard occurrence to the terms in Figure 16.1 for a chemical release:

Low: The probability of a hazard occurrence is considered unlikely during the expected lifetime of the facility assuming normal operation and maintenance.

Medium: The probability of a hazard occurrence is considered possible during the expected lifetime of the facility.

High: The probability of a hazard occurrence is considered sufficiently high to assume the event will occur at least once during the expected lifetime of the facility.

Definitions of severity regarding the *consequences* of a chemical release from a hazard occurrence as indicated in Figure 16.1 are as follows:

Low: The chemical is expected to move into the surrounding environment in negligible concentrations. Injuries are expected only for exposure over extended periods or when individual personal health conditions create complications.

Medium: The chemical is expected to move into the surrounding environment in concentrations sufficient to cause serious injuries and/or deaths unless prompt and effective corrective action is taken. Death and/or injuries are expected only for exposure over extended periods or when individual personal health conditions create complications.

High: The chemical is expected to move into the surrounding environment at concentrations sufficient to immediately cause serious injuries and/or deaths upon exposure. Large numbers of people are expected to be affected.

Once the system components and their failure modes have been identified, the acceptability of risks taken as a result of such failures must be determined. The risk assessment process yields more comprehensive and meaningful results when reliable statistical and probability data are available. In the absence of such data, the results are a strong function of the engineering judgment of the design team and must take into account both the severity and probability (frequency) of the accident if the results are to effectively aid the risk management process.

Table 16.3 summarizes another method of risk assessment that can be applied to an accidental system failure [10]. Both probability and consequence have been ranked on a scale of 0–1 with table entries in each cell being the sum of the corresponding probability and consequence value for that cell. The acceptability of risk is a major decision and can be described by

TABLE 16.3

Risk Data Summary

Probability ^a	Severity ^b									
	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0	1.1
0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0	1.1	1.2
0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0	1.1	1.2	1.3
0.4	0.5	0.6	0.7	0.8	0.9	1.0	1.1	1.2	1.3	1.4
0.5	0.6	0.7	0.8	0.9	1.0	1.1	1.2	1.3	1.4	1.5
0.6	0.7	0.8	0.9	1.0	1.1	1.2	1.3	1.4	1.5	1.6
0.7	0.8	0.9	1.0	1.1	1.2	1.3	1.4	1.5	1.6	1.7
0.8	0.9	1.0	1.1	1.2	1.3	1.4	1.5	1.6	1.7	1.8
0.9	1.0	1.1	1.2	1.3	1.4	1.5	1.6	1.7	1.8	1.9
1.0	1.1	1.2	1.3	1.4	1.5	1.6	1.7	1.8	1.9	2.0

^a Corresponds to ordinate in Figure 16.2.

^b Corresponds to abscissa in Figure 16.2.

dividing the situations presented in Table 16.3 into unacceptable, marginally acceptable, and acceptable regions. Figure 16.2 graphically represents the risk data from Table 16.3 using these three risk “acceptability” regions [11,12].

A final approach presented here for ranking the severity of a risk in terms of its consequence and likelihood of occurrence is shown in Table 16.4. Each cell in the matrix shown in Table 16.4 is assigned a risk ranking as indicated by the letters it contains. In this approach, an “A” level risk corresponds to a very severe consequence with a very high likelihood of occurrence. Action must be taken, and it must be taken promptly. At the other end of the scale, an “E” level risk is of little or no consequence with

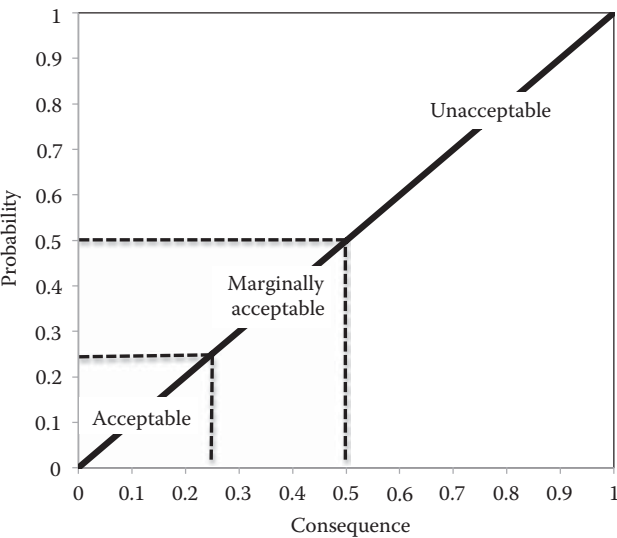


FIGURE 16.2
Graphical representation of risk data.

TABLE 16.4					
Ranking of Severity and Consequence					
Consequence	Likelihood of Occurrence				
	1	2	3	4	5
1	A	AB	B	BC	C
2	AB	B	BC	C	CD
3	B	BC	C	CD	D
4	BC	C	CD	D	DE
5	C	CD	D	DE	E

Consequence scale: 1, severe; 5, insignificant;
likelihood of occurrence scale: 1, very high
likelihood of occurrence; 5, very low likeli-
hood of occurrence.

a very low likelihood of occurrence, and no action is needed or justified. Other than risks classified as Level A or Level E, multiple combinations of consequence and likelihood of occurrence can result in similar risk levels. For example, a Level “C” risk be produced from a risk having little or no consequence but that has a very high likelihood of occurrence (5:1 in the Consequence:Likelihood of Occurrence matrix in Table 16.4), as well as from a risk having moderate consequences but only a moderate likelihood of occurrence (3:3 in the Consequence:Likelihood of Occurrence matrix in Table 16.4). Either of these Level “C” risk conditions might warrant mitigation with engineering and/or administrative controls or may represent risks that are acceptable with controls and adequate response procedures in place.

The reader is referred to Chapter 11 for additional qualitative approaches to risk assessment.

Illustrative Example 16.8

The occurrence of accident A at a chemical plant has an annual probability of 10^{-9} with consequences of 10^2 workers dying. Accident B’s annual probability is 10^{-6} with one person dying. Which scenario produces the higher risk? Justify the answer.

Solution

For Scenario A, the (annual) risk is:

$$\begin{aligned} &\text{Annual fatalities from Scenario A} \\ &= (10^{-9} \text{ accident/year}) (10^2 \text{ deaths/accident}) \end{aligned}$$

$$\begin{aligned} \text{Annual fatalities from Scenario A} &= 10^{-7} \text{ deaths} \\ &= 0.1 \times 10^{-6} \text{ deaths} \end{aligned}$$

For Scenario B, the (annual) risk is:

$$\begin{aligned} &\text{Annual fatalities from Scenario B} \\ &= (10^{-6} \text{ accident/year}) (10^0 \text{ deaths/accident}) \end{aligned}$$

$$\text{Annual fatalities from Scenario B} = 10^{-6} \text{ deaths} = 1 \times 10^{-6} \text{ deaths}$$

From these results, it is obvious that Scenario B produces a higher risk by a factor of 10. One could also classify Scenario A as a 1:5 or a C risk from Table 16.4, while Scenario B could be classified as a 3:2 or BC risk, making Scenario B the higher risk scenario.

16.7 Uncertainties/Limitations

The reader should note that this topic has been discussed in several earlier chapters in Parts II and III. Estimating the magnitude of risks that cannot be measured accurately or directly often requires employing assumptions that cannot be verified or tested experimentally. Obviously, knowledge about the present and the future is never completely accurate. Inadequate knowledge is usually the largest cause of uncertainty. The inadequacy of knowledge means that the full extent of the uncertainty is also unknown. Uncertainty due to variability occurs when a single number (as often employed in risk analysis) is used to describe something that truly has multiple or variable values. Variability is often ignored by using values based on the mean of all the values occurring within a group. Information on sources of uncertainties and limitations of input data are available in Ref. [13]. Some of this material is provided below.

Uncertainties and limitations in system description data could include the following:

1. Process description and/or drawings are incorrect or out of date.
2. Procedures do not represent actual operations.
3. Site area maps and population data may be incorrect or out of date.
4. Weather data from the nearest available site may be inappropriate due to its distance from the site or dissimilarity to microclimatic conditions.

Hazard identification data could have uncertainties and/or limitations because:

1. Recognition of major hazards may be incomplete.
2. Screening techniques employed for selection of hazards for further evaluation may omit important cases.

Consequence techniques may have sources of uncertainty or limitations due to calculational burdens (even with computers) that arise from a number of dispersion modeling variables including:

1. *Uncertainties in physical modeling* due to:
 - a. Inappropriate model selection
 - b. Incorrect or inadequate physical basis for model
 - c. Inadequate validation
 - d. Inaccurate model parameters

2. *Uncertainties in physical model data* due to:
 - a. Input data (composition, temperature, pressure)
 - b. Source terms for dispersion and other models
3. *Uncertainties in effects modeling* due to:
 - a. Animal data that may be inappropriate for humans (especially for toxicity)
 - b. Mitigating effects may be omitted
 - c. Lack of epidemiological data on humans of the same sex, age, education, etc.

Frequency techniques may have sources of uncertainty or limitations due to:

1. *Uncertainties in modeling* due to:
 - a. Extrapolation of historical data to larger scale operations that may overlook hazards introduced by scale-up to larger equipment
 - b. Limitation of fault tree theory that requires system simplification
 - c. Incompleteness in fault and event tree analysis
2. *Uncertainties in data* that may be caused because:
 - a. Data may be inaccurate, incomplete, or inappropriate
 - b. Data from related activities might not be directly applicable
 - c. Data generated by expert judgment may be inaccurate
 - d. Characterization of the general population is improper or incomplete

Risk estimation may have sources of uncertainty or limitations due to:

1. *Assumptions of symmetry* such as:
 - a. Uniform wind roses that rarely occur
 - b. Uniform ignition sources that may be incorrect
 - c. Single point source for all incidents that may be inaccurate
2. *Assumptions to reduce the complexity of the analysis* such as:
 - a. A single condition of wind speed and stability that may be too restrictive
 - b. A limited number of ignition cases that can reduce accuracy
 - c. General problems with the quality of data

The reader should note that since many risk assessments have been conducted on the basis of fatal effects, there are also uncertainties on precisely what constitutes a fatal dose of thermal radiation, blast effect, a toxic

chemical, etc. Where it is desired to estimate injuries as well as fatalities, the consequence calculation can be repeated using lower intensities of exposure leading to injury rather than death, but uncertainties regarding the accuracy of dose–response relationships in exposed populations remain. In addition, if the adverse health effect (e.g., associated with a chemical release) for both chronic and acute emissions and exposures is delayed, the cause may not be obvious, making it difficult to quantify such delayed effects both in the available risk data and in the results of the risk assessment.

Another problem with risk estimates is that they are usually based on very conservative assumptions. Thus, the analyses may result in a calculation that presents too high a risk. Unnecessary equipment or procedures may have to be installed/instituted at a facility to reduce the calculated risk. In an effort to better understand the significance of risk assessment, it is often helpful to place the estimated risks in perspective with other risks.

In an attempt to handle uncertainties and unknowns, Theodore [13] proposed a modified version of the standard Delphi panel approach that he has modestly defined as the Theodore Approach. As noted in Chapters 1 and 11, in order to generate “better” risk estimates, several knowledgeable individuals within and perhaps outside the organization are asked to independently provide estimates of risk, with explanatory details on these estimates. Each individual in the panel is then allowed to independently review all responses. The cycle is then repeated until the group’s responses approach convergence. The reader should once again note that despite such efforts to develop consensus on risk estimates, variability and inadequate input may occur at each stage in the risk assessment process.

Illustrative Example 16.9

What are the two concepts that generally arise in a discussion associated with uncertainty?

Solution

Generally, uncertainty consists of two parts: variability and inadequate knowledge. Uncertainty due to variability occurs when a single number is used to describe something that truly has multiple or variable values. Variability is often ignored by using values based on the mean of all the values occurring within a group. A second type of variability is when a single value exists but changes constantly over time.

Despite the importance of variability of data, inadequate knowledge is usually the largest cause of uncertainty. Three common sources of inadequate knowledge include:

1. Parameter uncertainty or lack of knowledge of accurate parameter values due to measurement errors, random errors, systematic errors, etc.

2. Model uncertainty due to errors arising from incorrect conceptions of reality and the use of incorrect models for describing chemical releases, transport, and exposures
3. Decision-rule uncertainty or lack of knowledge regarding how best to interpret modeling outcomes and resulting consequences

16.8 Quantitative Hazard Risk Assessment

This section reviews and develops quantitative methods for the assessment of hazard conditions in terms of the frequency of occurrence and unfavorable consequences. As with other risks, uncertainty in hazard risk assessment characterizes not only the transformation of a hazard into an accident, disaster, or catastrophe but also the effects of such a transformation on the exposed population and environment. The quantitative measurement of uncertainty falls within the purview of mathematical probability (see Chapter 14). Although Chapter 14 presents fundamental concepts and theorems of probability used in risk assessment, i.e., it discusses special probability distributions and techniques pertinent to risk assessment, the reader should note that the quantitative treatment of uncertainty is beyond the scope of this chapter.

Quantitative risk assessment usually produces single-number estimates. Although there are sufficient uncertainties associated with these quantitative numerical values, they serve a valuable function. These may be used to compare one risk with another in a quantitative sense, or they may be occasionally employed in an absolute sense.

A simple procedure that can be used for some quantitative estimates is to imagine all possible events that are required for an accident to occur. This procedure is codified in fault and event trees analysis discussed earlier in Chapters 14 and 15. For certain situations, the probability of an accident can be calculated as the product of individual probabilities:

$$P = P_1 P_2 P_3 P_4 \dots \quad (16.1)$$

Even limited historical data and tests on the numbers P_1 , P_2 , P_3 , and P_4 usually lead to results that give an extremely small overall probability.

In many applications the risk may be obtained by simply examining the frequency and consequence(s) associated with a hazard. The risk, R , consequence, C , and frequency, F , can be related through the equation:

$$R = (C)(F) \quad (16.2)$$

One of the most popular risk approaches employed by industry is the fatal accident rate (FAR) concept. FAR represents the number of fatal accidents per 1000 workers in a working lifetime (10^8 h), where a working lifetime for a single worker is assumed to be approximately 10^5 h. An acceptable FAR (by industry standards) is 4.0. This acceptable FAR is made up of:

1. Ordinary industrial risks with a FAR=2
2. Chemical risks with a FAR=2

In addition, industrial standards suggest that each individual chemical FAR risk should not exceed 0.4. Based on the aforementioned definition, if the hazard rate is the rate at which “dangerous” incidents occur, then the dangerous incident should not occur more often than:

$$\begin{aligned} &0.4 \text{ fatal accidents}/10^8 \text{ working hour} \\ &= 1.0 \text{ fatal accident}/2.5 \times 10^8 \text{ working hour} \\ &\oplus 1 \text{ fatal accident}/28,500 \text{ working years} \end{aligned}$$

This is approximately equivalent to 3.5×10^{-5} fatal accidents/year, i.e., the probability of occurrence should not exceed 3.5×10^{-5} (year) $^{-1}$. If a worker is killed every 10th time the incident occurs, then the target hazard rate is:

$$1 \text{ fatal accident}/285,000 \text{ working year} = 3.5 \times 10^{-6} \text{ fatal accidents/year}$$

For workers in a chemical plant, the FAR can be calculated as follows [13]:

$$FAR = \frac{10^8}{(8760 \text{ h/year})} (F) \left(\frac{D}{N} \right) \quad (16.3)$$

where

FAR is the fatal accident rate

F is the frequency of the event, year

D is the expected number of fatalities, given the event

N is the average number of exposed individuals on each shift

Finally, the total individual risk at each location is equal to the sum of the individual risks at that location from all incident outcome cases or:

$$IR_{x,y} = \sum_{i=1}^n IR_{x,y,i} \quad (16.4)$$

where

$IR_{x,y}$ is the total individual risk of fatality at geographical location x, y

$IR_{x,y,i}$ is the individual risk of fatality at geographical location x, y from incident outcome case i

n is the total number of incident outcome cases

There are a host of the other indices that are employed to measure risk. Although many of these were discussed earlier, the AIChE has provided two excellent references in this area [8,14].

This section concludes with a host of illustrative examples concerned with the calculation of risk. The examples range from simple analytical calculations to detailed calculational analysis.

Illustrative Example 16.10

Consider the following two “accident” scenarios:

Case A: One person is killed every year for 10 years.

Case B: Ten people are killed once every 10 years.

Should the risk concern for Case A have a higher priority than the risk concern for Case B?

Solution

Generally, priority would be given to Case B since the press, public, and elected officials would express greater concern for more fatalities occurring at a single time as compared to Case A. However, the risk in each case is 1 in 10, 0.1, or 10^{-1} on an annual basis.

Illustrative Example 16.11

It is estimated that an “accident” will occur once in 10 years, i.e., 10^1 years and will cause \$10,000,000, i.e., 10^7 damage. You have been requested to estimate the “maximum” amount of money that should be expended to prevent the accident based on this projected property damage.

Solution

The average annual cost for the accident is $10^7/10^1 = 10^6$ /year. Thus, you should spend a “maximum” of approximately \$1,000,000 annually, that is, 10^6 /year, to avoid the occurrence of this accident. If more money is spent than this amount each year, more money would be spent on mitigation efforts than would be saved.

Illustrative Example 16.12

Identify potential problem areas that may develop for a company if acceptable FAR numbers are exceeded.

Solution

Potential problems that may develop for a company within the community if acceptable FAR numbers are exceeded include the following:

1. Adverse publicity by the media
2. Adverse community relations
3. Decreased public trust in the company

Potential problems that may develop for a company based on resulting legal and regulatory issues if acceptable FAR numbers are exceeded include the following:

1. Legal action against the company by those affected
2. Potential notices of violations by appropriate regulatory agencies, i.e., National Institute of Occupational Safety and Health (NIOSH), Occupational Safety and Health Administration (OSHA), Environmental Protection Agency (EPA), etc.
3. Advisory actions regarding permit compliance

Potential problems that may develop for a company from employees if acceptable FAR numbers are exceeded include the following:

1. Employee safety concerns and discontent
2. Increased employee turnover
3. Decreased productivity

Potential problems that may develop for a company concerning economics and finances if acceptable FAR numbers are exceeded include the following:

1. Increased insurance costs
2. Decreased profits due to customer dissatisfaction
3. Decreased profits due to decreased employee productivity
4. Fines for violating regulations

If acceptable FAR numbers are not maintained within a company, a lack of concern for health and safety becomes apparent, and a multitude of problems, such as those listed above, can arise.

Illustrative Example 16.13

You have been hired as a consultant to an administrator who has a limited budget for the mitigation of hazards in a certain chemical plant. The plant employs two kinds of workers: day employees who work one 8h shift daily, and shift employees who rotate through three 8h shifts each day. A HAZOP–HAZAN report reveals that two kinds of accidents are possible during plant operation.

Accidents of the first kind result in the death of one day employee per incident and occur with a frequency of 2.92×10^{-5} accidents per

year. Accidents of the second kind result in the death of 100 shift workers per incident and occur with a frequency of 8.76×10^{-7} accidents per year.

1. Calculate the FAR for the first kind of accident. As noted earlier, the FAR is a measure of the risk associated with an accident or event in units of number of deaths/1000 worker lifetimes, or 10^8 h.
2. Calculate the FAR for the second kind of accident.

Solution

1. The FAR for the first type of accident is:

$$\begin{aligned} \text{FAR, accident Type 1} &= \left(\frac{1 \text{ Fatality}}{\text{Accident}} \right) \left(2.92 \times 10^{-5} \frac{\text{accidents}}{\text{year}} \right) \\ &\quad \times \left(\frac{1 \text{ year}}{365 \text{ days}} \right) \left(\frac{1 \text{ day}}{8 \text{ h}} \right) \left(\frac{10^8 \text{ h}}{1000 \text{ lifetimes}} \right) \end{aligned}$$

$$\text{FAR, accident Type 1} = 1 \text{ Fatality} / 1000 \text{ worker lifetimes}$$

2. The FAR for the second type of accident is:

$$\begin{aligned} \text{FAR, accident Type 2} &= \left(\frac{100 \text{ Fatalities}}{\text{Accident}} \right) \left(8.76 \times 10^{-7} \frac{\text{accidents}}{\text{year}} \right) \\ &\quad \times \left(\frac{1 \text{ year}}{365 \text{ days}} \right) \left(\frac{1 \text{ day}}{24 \text{ h}} \right) \left(\frac{10^8 \text{ h}}{1000 \text{ lifetimes}} \right) \end{aligned}$$

$$\text{FAR, accident Type 2} = 1 \text{ Fatality} / 1000 \text{ worker lifetimes}$$

The previous calculations indicate that both types of accidents have the same FAR. The consequences of these two types of accidents may be different, however, and are discussed in the next illustrative example.

Illustrative Example 16.14

Referring to the previous illustrative example, what considerations would influence your recommendation on the allocation of funds to reduce these Type 1 or Type 2 hazards?

Solution

While any answer to the question on the allocation of funds is likely to be incomplete, the following recommendation is suggested for further discussion.

Based on the previous calculations, the FARs for the two types of accidents are equal, and it is likely that over long periods of time an equal number of deaths may be expected from both types of accidents. This does not mean that equal consequences to the company will result from the two types of accidents, however. Accidents of the first type involve a low (but, perhaps, steady) loss of life. Accidents of the second type, however, are sure to attract more attention in the media. Adverse public relations are nearly certain, as well as unfavorable attention from legislators and other public officials.

Also, Type 2 accidents have a catastrophic effect on production. Not only will the entire facility be demolished (in all likelihood), but a large fraction of the pool of trained personnel will be lost all at once. Who will train replacement personnel if everyone is lost in the disaster? Similar concerns make disruption in the community much greater for Type 2. Some of these considerations can be factored into decision making based on direct economic losses that increase the burden of the Type 2 accident to both the company and the community.

One view (one that is the only acceptable view to many people) is to give priority to the prevention of both types of accidents.

Illustrative Example 16.15

Refer to Illustrative Examples 15.13 and 15.14. Calculate the risk associated with the radioactive emissions described in these illustrative examples.

Solution

Of the 1,110,000 people potentially affected by the radioactive emissions presented in Illustrative Examples 15.13 and 15.14, a total of 20 will die. The annual risk associated with the emission for all the potentially affected individuals is therefore:

$$\text{Annual risk} = 20/1,110,000 = 1.8 \times 10^{-5} = 18 \times 10^{-6}$$

With reference to Figure 15.4, the risk characterization step noted as “to be determined in Chapter 16” should now read 18×10^{-6} individuals will die annually.

The annual risk for each zone may also be calculated as follows:

$$\text{Risk (0 – 1 mile)} = 10/10,000 = 10^{-3}$$

$$\text{Risk (1 – 5 miles)} = 10/100,000 = 10^{-4}$$

$$\text{Risk (5 – 20 miles)} = 0.1/1,000,000 = 10^{-7}$$

Illustrative Example 16.16

Refer to Illustrative Examples 15.15 and 15.16. Calculate the risk associated with the individuals near the explosion center.

Solution

Since the annual probability of the explosion occurring is 10^{-6} , the annual risk on a number of fatalities and injuries basis is:

$$\begin{aligned} & (20 \text{ individuals killed within } 100 \text{ m of explosion center}) (10^{-6}/\text{year}) \\ & = 20 \times 10^{-6} \text{ fatalities/year} \end{aligned}$$

and

$$\begin{aligned} & (25 \text{ individuals severely injured within } 100 \\ & \quad - 200 \text{ m of explosion center}) (10^{-6}/\text{year}) \\ & = 25 \times 10^{-6} \text{ severe injuries/year} \end{aligned}$$

If the annual risk is based on the 145 potential affected individuals, 100 of which are outside the 200m severe injury effect radius, the resulting annual risks are

$$\begin{aligned} \text{Annual individual fatality risk} &= \frac{(20 \times 10^{-6} \text{ fatalities/year})}{145 \text{ individuals}} \\ &= 0.138 \times 10^{-6}/\text{year} \end{aligned}$$

$$\text{Annual individual severe injury risk} = \frac{(25 \times 10^{-6} \text{ severe injuries/year})}{145 \text{ individuals}}$$

$$\text{Annual individual severe injury risk} = 0.172 \times 10^{-6}/\text{year}$$

With reference to Figure 15.5, the risk characterization step noted as “to be determined in Chapter 16” should now read 0.138×10^{-6} will die and 0.172×10^{-6} will be severely injured.

Illustrative Example 16.17

Discuss the significance of Figure 16.3.

Solution

Figure 16.3 allows one to compare the cost of damage associated with an accident with the cost of increasing protection. As seen on the graph,

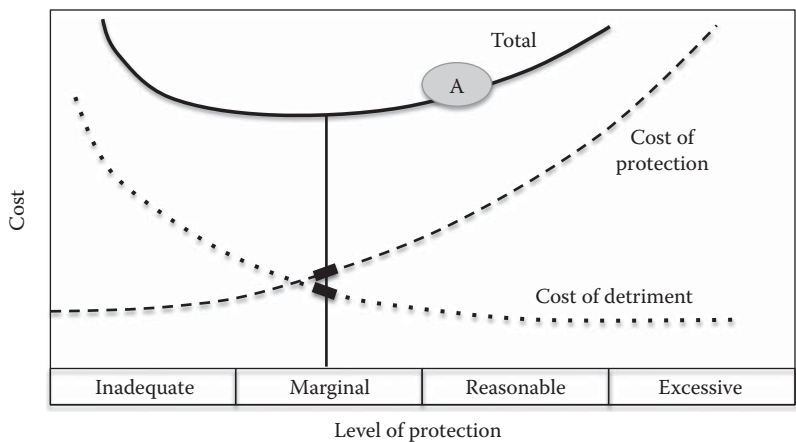


FIGURE 16.3
Accident cost/protection analysts.

for low levels of cost protection, the risk of damage or detriment costs are unreasonably high. However, for high levels of cost protection, the costs of detriment are significantly low. Therefore, a cost-benefit analysis should be performed in order to determine a reasonable cost for an acceptable level of protection while keeping the detriment costs to a minimum. From a plant’s perspective, the level of protection should be set at region A. From a purely economic point of view, this point represents the minimum cost. Other factors such as regulation requirements, good will, etc., can change this.

This illustrative example introduces the reader to the concept of a cost-benefit analysis. This approach involves comparing and balancing costs versus benefits, i.e., the cost to reduce/eliminate a risk problem, e.g., employing safety measures, versus the benefits associated with these risk reduction measures. One might view this as an analysis of money spent versus lives and property saved.

Illustrative Example 16.18

A train has collided with a truck at an intersection in the industrial area of a major city. A tank car and a flatbed car filled with containers have derailed. The tank car is lying in a ditch alongside the tracks surrounded by some containers that have broken loose from the flatbed car. The following information is known:

1. The tank car is labeled “hydrogen fluoride.”
2. The United Nations North America (UNNA) number shown on all the containers is 1806. (The UNNA numbering system was developed by the U.S. Department of Transportation and has since become the UN standard system for classifying hazardous materials.)

If you were responding to this incident, what additional information would you want to know to assist in the risk characterization and risk management/mitigation activities that will be required at this accident site?

Solution

The following additional information will be necessary in the risk characterization and mitigation effort:

1. Physical, chemical, and toxicity information (particularly health related) on hydrogen fluoride.
2. The chemical in the containers spilled from the flatbed from the UNNA number on the containers. The number 1806 represents phosphorus pentachloride.
3. Physical, chemical, and toxicity information (particularly health related) on phosphorus pentachloride.
4. Determine what problems could occur if hydrogen fluoride and phosphorus pentachloride were to be *mixed* together when crews right the tank car and recover the containers.

Illustrative Example 16.19

Explosion concerns have arisen regarding the location and operation of a gasoline storage terminal. A HAZOP analysis followed by an ETA and FTA produced the data:

Annual probability of explosion = 4×10^{-5}

Number of individuals located at that the storage facility = 20

Number of additional individuals located at the terminal but away from the storage facility = 200

All individuals at the storage facility die if an explosion occurs. A total of 20% of all individuals at the terminal die if an explosion occurs, while the balance (80%) are severely injured. No one "outside" the terminal fence is affected by the explosion.

Perform a hazard risk assessment, including risk calculations for all potentially affected individuals.

Solution

Determine the total number of people who will die annually due to the potential explosion. This number, measured in terms of the annual total number of people killed, is obtained by multiplying the number of people in each impact zone by the probability of the event affecting that zone and summing the results. Thus, for the potential gasoline storage terminal explosion,

$$\begin{aligned} \text{Total fatalities} &= 20 \text{ (at the storage facility)} \\ &+ (200 \text{ in terminal}) (0.2 \text{ fraction of fatalities}) \end{aligned}$$

Total fatalities = 20 + 40 = 60 fatalities due to a storage tank explosion

$$\begin{aligned}\text{Total annual fatalities} &= (60 \text{ fatalities/event}) (4 \times 10^{-5} \text{ events/year}) \\ &= 240 \times 10^{-5}\end{aligned}$$

$$\text{Total annual fatalities} = 2.4 \times 10^{-3} / \text{year}$$

The *average annual individual risk*, AAIR, for all the individuals within the terminal boundary (fence) is based on 220 individuals. Thus,

$$\text{AAIR of fatality} = \frac{2.4 \times 10^{-3}}{220} = 1.1 \times 10^{-5} = 11 \times 10^{-6} / \text{year}$$

Similarly,

$$\begin{aligned}\text{Total severely injured} \\ &= (200 \text{ in terminal}) (0.8 \text{ fraction of severe injuries}) + 0\end{aligned}$$

$$\begin{aligned}\text{Total severely injured} \\ &= 160 \text{ severe injuries due to a storage tank explosion}\end{aligned}$$

Total annual severe injuries

$$= (160 \text{ severe injuries/event}) (4 \times 10^{-5} \text{ events/year}) = 6.4 \times 10^{-3} / \text{year}$$

$$\text{AAIR of severe injury} = \frac{6.4 \times 10^{-3}}{220} = 2.9 \times 10^{-5} = 29 \times 10^{-6} / \text{year}$$

Illustrative Example 16.20

Translate the data and results of the previous example on to a figure similar to that provided in Figures 4.2 and 12.1.

Solution

See Figure 16.4

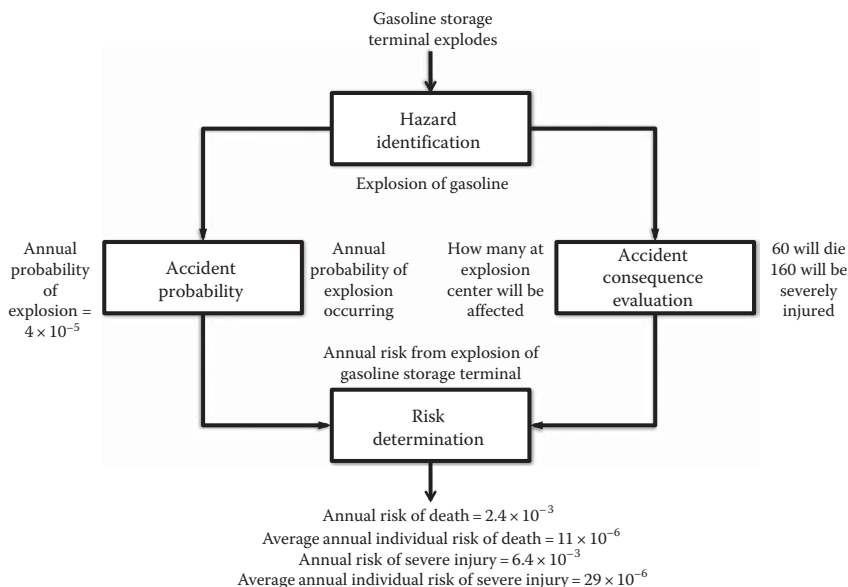


FIGURE 16.4

Storage terminal hazard risk assessment for Illustrative Example 16.20.

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Part IV

Case Studies

Revolutions break out when opposite parties, the rich and the poor, are equally balanced, and there is little or nothing between them; for, if either party were manifestly superior, the other would not risk an attack upon them.

Aristotle (384–322 BC)

Politics, Book V

When we risk no contradiction, It prompts the tongue to deal in fiction.

John Gay (1688–1732)

Fable, Part I, The Elephant and the Bookseller

A flatterer can risk everything with great personages.

Alain Rene Le Sage (1668–1747)

Gil Blas, Book IV, Chapter 7

17

The Case for Case Studies

17.1 Introduction

Over the past 15 years, the authors have used case studies to discuss risk issues in the engineering and scientific professions. Having done this separately in course offerings and jointly with others in environmental and chemical engineering seminars, the authors believe that the case method is one of the best ways to engage students and professionals in the discussion of risks facing the engineering and scientific communities. The authors also feel that individuals are more committed to the learning process if they prepare cases themselves.

This case study portion of the book is the result of the authors' experience with the case study method, and the enthusiasm and imagination of the case authors, some of whom were students in the School of Engineering at Manhattan College. Nearly all these cases address issues in environmental risk. They are categorized under four headings:

1. Monte Carlo Simulation (Chapter 18)
2. Emergency Planning and Response (Chapter 19)
3. Natural Disasters (Chapter 20)
4. Industrial Accidents (Chapter 21)

The cases address issues of interest in four engineering fields: chemical, civil, environmental, and mechanical engineering.

This case study material is a valuable resource for both practitioners and academics. Academics as well as business and industry leaders—whether at the level of chief executive officer or in a line position—will find these cases helpful in calculating, understanding, predicting, and evaluating risk concerns. Thus, it will help professionals in the field and educators in the classroom to better focus their discussion on risk issues. Engineering and science faculty will find this material an excellent source of risk-related information because it provides a set of cases that can assist the professor in integrating risk issues into a wide variety of courses. While also helping

to satisfy accreditation requirements, this approach enables the teacher to address health and hazard risk assessment issues throughout various courses since the cases individually do not require significant time commitments. These discussions will help make a lasting impression on future engineers and scientists [1].

17.2 Case Study Criteria: Is It Logical, Relevant, and Reasonable?

There are four major criteria that should be present and addressed in any meaningful case study. These are detailed in the following:

1. *Logically consistent.* The case study reader should be introduced to the importance of consistency in any discussion of risk. Good arguments do not assert some claim as both true and false simultaneously. Contradictions may make interesting brainteasers, but they usually do not help make good arguments.
2. *Relevant criteria.* The preparer should be encouraged to include as much information that is relevant to their case as possible and not to leave things out. Even if one knows that something is relevant but problematic to a particular position, better he or she should introduce the criteria and explain why it is problematic than to ignore it completely.
3. *Irrelevant criteria.* In addition to *relevant criteria*, the preparer should carefully consider what not to include in their arguments. Appeals to emotion, in particular, when dealing with risk are often less helpful and more likely to be irrelevant than appeals to reason. Extraneous information should be avoided.
4. *Reasonable argument.* A case study that is logically consistent, includes all the relevant information, and excludes irrelevant considerations. Nonetheless, it must also be reasonable to be a good risk argument and/or discussion. Note that being reasonable does not necessarily mean that everyone has to agree with the premise set forth in the case study.

17.3 Preparing a Case Study Solution

The development and preparation of a case study can be accomplished alone or in groups of three to five. One needs to consider the role that consensus

plays in the preparation as opposed to a single individual who must articulate a unified position. It is during the preparation stage that the real learning can happen. As students struggle to explain answers to complex issues and risk dilemmas, they will hopefully arrive at a consensus. The reader may also choose to treat the case studies as additional essay material, similar to that presented in Parts I through III [1].

Case studies were designed to bring a mix of learning and (occasionally) entertainment to what may be perceived as a dull and irrelevant subject. The “spectacle” of a case study can enliven this subject and help readers begin to address the importance of risk decision making. Depending on the level of preparation, the case study can provide the beginner students, who might otherwise be uninterested, and thus less likely to seek out risk details and information, with an innovative supplement to the traditional study of health risk and hazard risk assessment [1].

The case studies presented in the following chapters are stand-alone examples and may be viewed as expanded illustrative examples. Every attempt has been made to relate these studies to the simple health risk assessment algorithms provided in Figure 7.1 and the hazard risk assessment algorithm presented in Figure 12.1.

Reference

1. Adapted from J. Wilcox and L. Theodore, *Engineering and Environmental Ethics: A Case Study Approach*, John Wiley & Sons, Hoboken, NJ, 1998.

18

Monte Carlo Simulation

18.1 Introduction

The first case study chapter deals with a somewhat unique approach to dealing with difficult problems. Monte Carlo simulation is a procedure for mimicking observations on a random variable that permits verification of results that would ordinarily require difficult mathematical calculations or extensive experimentation to achieve. The method normally uses variable values produced by *random number generators*. A random number is a number selected from the interval (0,1) in such a way that the probabilities that the number comes from any two subintervals of equal “length” are equal. For example, the probability that the number is in the subinterval (0.1,0.3) is the same as the probability that the number is in the subinterval (0.5,0.7). Thus, random numbers are observations on a random variable X having a uniform distribution in the interval (0,1). This means that the probability distribution function (pdf), described in Chapter 14, of X is specified by:

$$\begin{aligned} f(x) &= 1; & 0 < x < 1 \\ &= 0; & \text{elsewhere} \end{aligned} \tag{18.1}$$

This pdf assigns equal probability to subintervals of equal length in the interval (0,1). Using random number generators, Monte Carlo simulation can generate observed values of a random variable having any specified pdf. For example, to generate observed values of T , the time to failure, when T is assumed to have a pdf specified by $f(t)$, one first uses a random number generator to generate a value of T between 0 and 1. The solution is an observed value of the random variable T having a pdf specified by $f(t)$ [1].

This chapter is highlighted with four case studies that are concerned with lifetime, failure, and failure-related calculations. The reader is encouraged to extend these results to the determination of hazard risk information. The four cases are as follows:

Time to pump failure

Times to failure of two electrical components

Nuclear plant temperature gauge lifetime

Bus section failures in electrostatic precipitators

18.2 Case Study 1: Time to Pump Failure

A pump in a petrochemical facility has a time to failure, T , measured in *years*, with an exponential pdf (see also Chapter 14) specified by:

$$\begin{aligned} f(t) &= e^{-t}; \quad t > 0 \\ &= 0; \quad \text{elsewhere} \end{aligned} \quad (18.2)$$

1. Generate 15 simulated values of T using a Monte Carlo procedure, i.e., the generation of random numbers.
2. Use the results of Part 1 to estimate the average life of the pump.
3. Outline at least two other methods that could be employed to estimate the average life of the pump in Part 1.

Solution

1. Calculate the cumulative distribution function (cdf), $F(t)$, from the given pdf specified by $f(t)$, that is,

$$\begin{aligned} f(t) &= e^{-t}; \quad t > 0 \\ &= 0; \quad t \leq 0 \end{aligned} \quad (18.3)$$

Applying Equation 18.3 to a cdf, one may write:

$$\begin{aligned} F(t) &= P(T \leq t) = \int_0^t f(t) dt \\ &= \int_0^t e^{-t} dt \\ &= 1 - e^{-t}; \quad t > 0 \\ &= 0; \quad t \leq 0 \end{aligned} \quad (18.4)$$

Fifteen random numbers are now generated in the interval or range of 0–1:

0.93
0.06
0.53
0.56
0.41
0.38
0.78
0.54
0.49
0.89
0.77
0.85
0.17
0.34
0.56

For each random number generated, solve Equation 18.4 for t by setting the random number equal to $F(t)$. For example, the first random number generated is 0.93. Setting this equal to the cdf, $F(t)$, produces the equation:

$$0.93 = 1 - e^{-t}$$

Solving yields

$$e^{-t} = 0.07$$

$$t = -\ln 0.07 = 2.66$$

Therefore, the first simulated value of T , time to failure, is 2.66 years. The other simulated values of T obtained in the same manner are shown in Table 18.1.

2. The average value of the 15 simulated values of T obtained by dividing the sum by 15 is 1.02 years; this represents the Monte Carlo estimate of the average life of the pump.
3. The exact value of the average life of the pump can be calculated by finding the expected value of T from its pdf as shown in Equation 18.5 [1]:

$$E(T) = \int_{-\infty}^{\infty} tf(t)dt \quad (18.5)$$

TABLE 18.1
Simulated Time to Failure
for Case Study 1

Random Number	Simulated Time to Failure (Years)
0.93	2.66
0.06	0.06
0.53	0.76
0.41	0.82
0.38	0.48
0.78	1.52
0.54	0.78
0.49	0.67
0.89	2.21
0.77	1.47
0.85	1.90
0.17	0.19
0.34	0.42
0.56	0.82

Applying Equation 18.5 by substituting and integrating leads to:

$$\begin{aligned} E(T) &= \int_{-\infty}^{\infty} te^{-t} dt \\ &= 1.0 \end{aligned}$$

A more accurate estimate of the true value of the average life of the pump can be obtained by increasing the number of simulated values on which the estimate is based. The expected value, or mean, can be shown to be equal to the coefficient associated with the exponential term, i.e., (1) *t*, for an exponential distribution. Therefore, the mean for this distribution is 1.0.

From a case study perspective, the merits of the approach to be employed should be discussed.

18.3 Case Study 2: Time to Failure of Two Electrical Components

A *series* system in a NASA spaceship consists of two electrical components, *A* and *B*. Component *A* has a time to failure, *T_A*, assumed to be normally distributed with a mean (μ)=100 months and a standard deviation (σ)=20 months. Component *B* has a time to failure, *T_B*, assumed to be normally

distributed with a mean = 90 months and standard deviation = 10 months. The system fails whenever either component *A* or component *B* fails. Therefore, T_s , the time to failure of the system, is the *minimum* of the times to failure of components *A* and *B*.

Estimate the average value of T_s on the basis of 10 simulated values of T_A and 10 simulated values of T_B .

Solution

First, generate 20 random numbers in the range of 0–1:

A	B
0.10	0.92
0.54	0.86
0.42	0.45
0.02	0.38
0.81	0.88
0.07	0.21
0.06	0.26
0.27	0.51
0.57	0.73
0.80	0.71

Use the table of the standard normal distribution [1], Table 14.1 in Chapter 14 and obtain the simulated value of Z corresponding to each of the random numbers. The first random number is 0.10; the corresponding simulated value of Z is -1.28 since the area under a standard normal curve to the left of -1.28 is 0.10. The remaining simulated values of Z are obtained in a similar fashion. The 20 simulated values of Z are provided in Table 18.2.

Using the first 10 simulated values of Z , obtain 10 simulated values of T_A by multiplying each simulated value of Z by 20 (the standard deviation, σ) and adding 100 (the mean, μ), that is, $T_A = \sigma Z + 100$, since Z can be expressed as follows (refer to Chapter 14 for details):

$$Z = \frac{T_A - 100}{\sigma} \quad (18.6)$$

Note that the lifetime or time to failure of each component, T , is calculated using this equation. Thus, multiplying each of the first 10 simulated values of Z by 20 and adding 100 yields the following simulated values of T_A :

74
102
96
59

TABLE 18.2
Simulated Values of Z for Case Study 2

Electrical Component	Random Number	Simulated Values of Z
A	0.10	−1.28
	0.54	0.10
	0.42	−0.20
	0.02	−2.05
	0.81	0.88
	0.07	−1.48
	0.06	−1.56
	0.27	−0.61
	0.57	0.18
	0.80	0.84
B	0.92	1.41
	0.86	1.08
	0.45	−0.13
	0.38	−0.31
	0.88	1.17
	0.21	−0.81
	0.26	−0.64
	0.51	0.03
	0.73	0.61
	0.71	0.56

118
70
69
88
104
117

Multiplying each of the second set of 10 simulated values of Z by 10 and adding 90 yields the following simulated values of T_B :

104
101
89
87
102
82
84
90
96
96

TABLE 18.3

Minimum Simulated Values for Case Study 2

Simulated Time to Failure (Months)		
Component A (T_A)	Component B (T_B)	System (T_S)
74	104	74
102	101	101
96	89	89
59	87	59
118	102	102
70	82	70
69	84	69
88	90	88
104	96	96
117	96	96

Simulated values of T_S corresponding to each pair of simulated values of T_A and T_B are obtained by recording the *minimum* of each pair. The values are shown in Table 18.3. The average of the 10 simulated values of T_S is 84 months, the estimated time to failure of the system.

The discussion for this case study should focus on whether 84 months, or 7 years, is acceptable for this NASA space endeavor.

18.4 Case Study 3: Nuclear Plant Temperature Gauge Lifetime

According to state regulations and Nuclear Regulatory Commission (NRC) rules, three temperature gauges (A , B , C) are required to be positioned near the outlet of a nuclear reactor. Assume that the individual temperature gauge component lifetimes are normally distributed with means and standard deviations given in Table 18.4.

Using the 10 random numbers from 0 to 1 provided in Table 18.5 for each temperature gauge, simulate the lifetime (time to temperature gauge failure) of the temperature recording system and estimate its mean and standard deviation, along with the estimated time to failure for this system. The lifetime is defined as the time (in weeks) for one of the temperature gauges to “fail.”

TABLE 18.4

Temperature Gauge Data for Case Study 3

Thermometer	A	B	C
Mean (months)	100	90	80
Standard deviation (months)	30	20	10

TABLE 18.5

Temperature Gauge
Random Numbers for
Case Study 3

For A	For B	For C
0.52	0.77	0.14
0.80	0.54	0.39
0.45	0.96	0.06
0.68	0.02	0.86
0.59	0.73	0.87
0.01	0.67	0.90
0.50	0.31	0.28
0.29	0.34	0.51
0.34	0.00	0.56
0.46	0.48	0.82

Solution

Let T_A , T_B , and T_C denote the lifetimes of temperature gauges A , B , and C , respectively. Let T_S denote the lifetime of the system. The random number generated in Table 18.5 may be viewed as the cumulative probability, and the cumulative probability is the area under the standard normal distribution curve. Because the standard normal distribution curve is symmetrical, the negative values of Z and the corresponding area are once again found by symmetry (see also Chapter 14). For example, as described earlier,

$$P(Z < -1.54) = 0.062$$

$$P(Z > 1.54) = 0.062$$

$$P(0 < Z < 1.54) = 0.5 - P(Z > 1.54)$$

$$= 0.5 - 0.062$$

$$= 0.438$$

Recall from the previous case study that the lifetime or time to failure of each component, T , is calculated using the equation:

$$T = \mu + \sigma Z \quad (18.7)$$

where

μ is the mean

σ is the standard deviation

Z is the standard normal variable

First, determine the values of the standard normal variable, Z , for temperature gauge A using the 10 random numbers given in the problem statement and the standard normal table. Then calculate the lifetime of temperature gauge A , T_A , using the equation for T given in the preceding equation (see Table 18.6).

Next, determine the values of the standard normal variable and the lifetime of temperature gauge B (see Table 18.7). Also, determine the values of the standard normal variable and the lifetime of temperature gauge C (see Table 18.8).

For each random value of each component, determine the temperature gauge system lifetime, T_S . Because this may be viewed as a “series system,”

TABLE 18.6
Lifetime of Temperature Gauge A (T_A) for
Case Study 3

Random Number	Z (from Standard Normal Table)	$T_A = 100 + 30Z$
0.52	0.05	102
0.80	0.84	125
0.45	-0.13	96
0.68	0.47	114
0.59	0.23	107
0.01	-2.33	30
0.50	0.00	100
0.29	-0.55	84
0.34	-0.41	88
0.46	0.10	97

TABLE 18.7
Lifetime of Temperature Gauge B (T_B) for
Case Study 3

Random Number	Z (from Standard Normal Table)	$T_B = 90 + 20Z$
0.77	0.74	105
0.54	0.10	92
0.96	1.75	125
0.02	-2.05	49
0.73	0.61	102
0.67	0.44	99
0.31	-0.50	80
0.34	-0.41	82
0.00	-3.90	12
0.48	-0.05	89

TABLE 18.8
Lifetime of Temperature Gauge C (T_C) for
Case Study 3

Random Number	Z (from Standard Normal Table)	$T_C = 80 + 10Z$
0.14	-1.08	69
0.39	-0.28	77
0.06	-1.56	64
0.86	1.08	91
0.87	1.13	91
0.90	1.28	93
0.28	-0.58	74
0.51	0.03	80
0.56	0.15	81
0.82	0.92	89

TABLE 18.9
Temperature Gauge System Lifetime
(Months) for Case Study 3

T_A	T_B	T_C	T_S
102	105	69	69
125	92	77	77
96	125	64	64
114	49	49	49
107	102	91	91
30	99	30	30
100	80	74	74
84	82	80	80
88	12	12	12
97	89	89	89
Total			635

the system lifetime is limited by the temperature gauge with the *minimum* lifetime (see Table 18.9).

The mean value, μ , of T_S is

$$\mu = \frac{635}{10} = 63.5 \text{ months}$$

Calculate the standard deviation, σ , of T_S using the equation [1]:

$$\sigma^2 = \frac{1}{n} \sum (T_S - \mu)^2 \tag{18.8}$$

TABLE 18.10

Temperature Gauge Standard
Deviation Calculations for
Case Study 3

System Lifetime (T_s)	$(T_s - \mu)^2$
69	30.25
77	182.25
64	0.25
49	210.25
91	756.25
30	1122.25
74	110.25
80	272.25
12	2652.25
89	650.25
Total	5987

where n is 10, the number values in the population. Note that this is not a sample, so that the modified form of Equation 18.8 presented in Ref. [1] applies for σ^2 (see Table 18.10).

Therefore,

$$\sigma = \left(\frac{5987}{10} \right)^{0.5} = 24.5 \text{ months}$$

A discussion on whether to continue to operate with two or perhaps only one temperature gauge in the nuclear reactor facility should be included in the case study discussion.

18.5 Case Study 4: Bus Section Failures in Electrostatic Precipitators

Theodore et al. [2] employed Monte Carlo methods in conjunction with the binomial and Weibull distributions discussed in Chapter 14 to estimate out-of-compliance probabilities for electrostatic precipitators (air pollution control particulate control devices) on the basis of observed bus section failures. The following definitions apply (see Figure 18.1):

Chamber. One of many passages (M) for gas flow

Field. One of several high voltage sections (N) for the removal of particulates; these fields are arranged in series (i.e., the gas passes from the first field into the second, etc.)

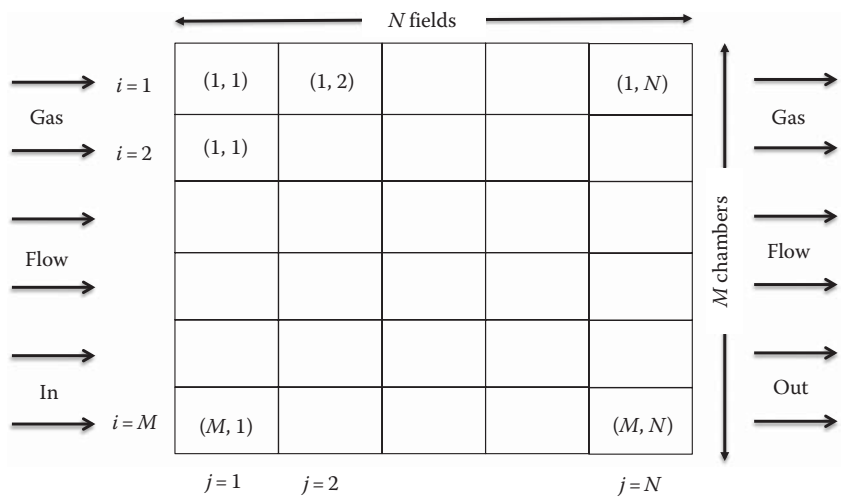


FIGURE 18.1
An $M \times N$ precipitator for Case Study 4.

Bus section. A region of the precipitator that is independently energized; a given bus section can be identified by a specific chamber and field

Thus, an $M \times N$ electrostatic precipitator consists of M chambers and N fields. A precipitator is “out of compliance” when its overall collection efficiency falls below a designated minimum value because of bus section failures. When several bus sections fail, the effect of the failures depends on where they are located. To determine directly whether a precipitator is out of compliance after a given number of bus sections have failed, it would be necessary to test all possible arrangements of the failure locations. The out-of-compliance probability is then given by the percent of arrangements that result in overall collection efficiencies less than the prescribed minimum standard. The number of arrangements to be tested often makes the direct calculation approach impractical. For example, Theodore et al. [2] were requested (as part of a consulting assignment) to investigate a precipitator unit consisting of 64 bus sections; if 4 of these were to fail, there would be 15,049,024 possible failure arrangements.

Instead of the direct calculation approach that would have required the evaluation of more than 15×10^6 potential failure arrangements, Theodore et al. [2] used a Monte Carlo technique, testing only a random sample of the possible failure arrangements. The arrangements to be chosen were selected by use of random numbers. A set of random numbers was generated equal in quantity to the number of bus section failures assumed. Each of the random numbers was used to identify a bus section that, during the calculation of overall collection efficiency, was assumed to be out of commission. A total of 5000 failure location arrangements were sampled for all the

TABLE 18.11Observed Bus Section Failures in 5×8 Precipitator for Case Study 4

Failure Number	Location (Chamber, Field)	Time to Failure (Days from Last Outage)
1	(4, 2)	62
2	(7, 4)	112
3	(8, 1)	153
4	(1, 3)	209

out-of-compliance probabilities calculated. The random numbers used were generated by the power residue method [3].

A leading utility in the northeast had also requested out-of-compliance information to better schedule outages (plant shutdowns). The time to failure, T , of a bus section was assumed to have a Weibull distribution, the parameters of which were estimated by the method of maximum likelihood on the basis of observed bus section failures shown in Table 18.11 for the utility's 5×8 precipitator [4]. The probability that the precipitator would be out of compliance after 330 days, at which time a plant outage had been scheduled, was calculated assuming that: (1) the last failure had just occurred and (2) 3 weeks had passed without the occurrence of another failure.

For each of the 36 bus sections that had not already failed, the Weibull distribution was used to determine the probability of their failure before the next outage. Under assumption (1), this probability is $P(T < 330 | T > 209)$, i.e., the conditional probability of failure before 330 days, given that the bus section has survived 209 days. Under assumption (2), the corresponding probability is $P(T < 330 | T > 230)$. Based on assumption (2), the estimates of the Weibull distribution parameters generated from assumption (1) were modified to take into consideration the absence of failures for three additional weeks.

Assuming a binomial distribution for the number of additional failures before the next outage, with the probability of success equal to $P(T < 330 | T > 209)$ based on assumption (1), the probability of success equal to $P(T < 330 | T > 230)$ based on assumption (2), and $n = 36$, the probabilities of 0, 1, 2, ..., 36 failures were calculated [1]. On the basis of those probabilities, the Monte Carlo method was used to estimate out-of-compliance probability as follows. For each run, a random number was generated that selected a failure number between 0 and 36 with the probability calculated as described earlier. Then, a set of random numbers was generated equal in number to the failure number selected. As described previously, each of these random numbers was used to identify a bus section that, during the calculation of overall collection efficiency, was assumed to be out of commission. After 5000 runs, the percentage of runs yielding an overall collection efficiency less than the prescribed standard was the estimated out-of-compliance

TABLE 18.12
Out-of-Compliance Probabilities for 5 × 8 Precipitator
for Case Study 4

Time (Days) from Last Failure	Operating Period (Days)	Out-of-Compliance Probability
0	330	0.504
	300	0.271
	270	0.095
21	330	0.181
	315	0.116
	300	0.066

probability. Table 18.12 shows the results for Assumptions (1) and (2) and also the effect of reducing the duration of the operating period (time between outages). Additional information on electrostatic precipitators is available in Refs. [5,6].

Discussion for this case study could center on the advantages/disadvantages of electrostatic precipitators, and the role other air pollution control equipment play in environmental management.

References

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6. L. Theodore, *Air Pollution Control Equipment Calculations*, John Wiley & Sons, Hoboken, NJ, 2008.

19

Emergency Planning and Response

19.1 Introduction

This chapter discusses four emergency planning and response case studies. Each of the first three cases were prepared and originally submitted in 2002 by a chemical engineering senior student at Manhattan College as part of an assignment for Course 528—"Accident and Emergency Management." The submitted assignments were later edited by the authors in 2011. The four cases presented in this chapter are:

Case Study 1: Terrorist attack of a pharmaceutical company's plant in Greenpoint, Brooklyn, NY

Case Study 2: Terrorist attack of the Brooklyn Navy Yard in Greenpoint, Brooklyn, NY

Case Study 3: Plans to counter the possibility of a process or plant-related accident at the "Wedo" chemical facility in Suffolk County, Long Island, NY

Case Study 4: Dilution ventilation models

19.2 Case Study 1: Terrorist Attack of a Pharmaceutical Company's Plant in Greenpoint, Brooklyn, New York

The world has recently been reminded of the serious threat that terrorism poses to society. In the wake of the horrific events that transpired on September 11, 2001, Ragona Associates has been asked to develop a plan to counter the possibility of a terrorist attack at a pharmaceutical plant located in Greenpoint, Brooklyn, NY [1].

Solution

Terrorism is not a simple issue to analyze. There are groups of professional terrorists in the world whose life's work is devoted to the destruction of society. These are highly motivated, well-trained, and very effective people. For these selected groups, there is always a possibility for the circumvention of safeguards designed to counter terrorism. The allocation of funds toward managing counter measures to such attacks is difficult to optimize due to the wide range of attacks that are possible. The paradox is that while one can never be too prepared for such an attack, overpreparation is an expensive and inefficient use of societal resources. Thus, it becomes necessary to determine what areas require priority attention by quantifying the probability and the consequences associated with different types of terrorist attacks on specific high-value or high-profile targets.

The potential for disaster is an everyday hazard in a pharmaceutical plant. Highly toxic materials are processed in these facilities day after day, and these facilities must be viewed as a potential target for terrorism. On the right day, with the right weather conditions, a toxic release from a pharmaceutical plant can be catastrophic to the plant site and/or to the areas surrounding the plant. This makes a pharmaceutical plant a rather attractive target for terrorists. Steps can be taken to counter such an attack. The inventory stored on site can be checked routinely (and perhaps randomly) to ensure that there are no foreign chemicals present that could have been placed there specifically to cause a violent reaction in a manufacturing process, resulting in an explosion and release of toxic materials. This may not be practical due to a large inventory and/or a high turnover rate. However, some sort of effort will at least demonstrate that the pharmaceutical company is not blind to the possibilities that are present. These details are presented in the discussion that follows.

For safe practice purposes, the inventory should be well managed and the amount of chemicals stored on site should be kept to a minimum to reduce the amount of chemicals that could be released or that could become involved with a release, fire, or explosion due to an attack or other plant mishap/accident.

The procedures governing the delivery and shipping of chemicals to and from the plant should be strictly managed. An effective measure for controlling such practices may be the incorporation of an airplane-like "black box" recording device that transmits to a receiver in the event of a delivery truck being commandeered by terrorists. This could be regulated by federal agencies and could be required for all transportation vehicles carrying a certain class of chemical. A pharmaceutical company may consider petitioning the government to create such a chemical tracking system.

Containment should be critically analyzed. This includes analysis both from an inventory and a processing perspective. The processes, as well as individual units located at a pharmaceutical plant or any chemical plant for

that matter, are often under considerable pressure, presenting the possibility for an explosion. This makes the pieces of equipment themselves targets. Pharmaceutical plants are typically operated on a smaller scale than are chemical plants allowing for the possibility of the total enclosure of the equipment to, in effect, shield the equipment from a possible attack. Whether or not there are materials available that are strong enough to withstand, say, a plane crash should be considered. However, even a barrier as simple as a brick wall would aid in preventing someone from shooting a hole into a pressurized vessel.

Perhaps, the more important area to devote the company's resources toward is the emergency response to a terrorist attack. As mentioned earlier, there are professional terrorists who will stop at nothing, even sacrificing their own lives, to succeed in an attack. As a result, there is always the possibility of an attack. The consequences of such an attack need to be considered and efforts must be made to minimize such consequences. Plans should be prepared for combating an explosion and for combating a toxic release. Specialized teams should be assembled and trained to accomplish such tasks. Worst-case scenarios should be drawn up and employees on site should be trained in how to conduct themselves during these scenarios. This training should be tested periodically. The extent of public exposure should be modeled for the worst-case release and a means of communicating a required evacuation of adjacent residences and businesses should be planned.

Perhaps the best method for countering terrorism for a pharmaceutical plant is to eliminate, if possible, the characteristics that make it an attractive target for terrorism. The plant should seek out chemicals and/or processes that are not hazardous and use them as alternatives to existing materials and methods. The location for the plant should be such that the worst-case release does not endanger human life.

A discussion of other options should be included in this case study.

19.3 Case Study 2: Terrorist Attack of the Brooklyn Navy Yard in Greenpoint, Brooklyn, New York

The Brooklyn Navy Yard is presently a 300 acre, 3.8 million square feet, industrial complex on the waterfront [2] and provides a panoramic view of New York Harbor (including the Statue of Liberty) and the New York City skyline. It consists of four operating docks and five piers active with maritime industrial use. There are presently over 3000 people working in the Navy Yard, and it houses more than 200 plants and businesses. There is also a 24h security system, but because of recent increased awareness of terrorism, there is need for additional security. Develop an emergency response plan for this facility.

Solution

To counter terrorist acts, a single phone number and emergency response organization for the Navy Yard area should be established for recording, analyzing, and responding to potential terrorist-related activities occurring in public areas that workers might observe in the normal course of their daily routines. This would also avoid overburdening the 911 system. The plant would be given printed materials on how to contact the reporting center and would in turn directly provide information and any training to their workers.

At the outset of the program, the postal and utility industries would also be encouraged to participate because their workers maintain regular public routes in the communities they serve, putting them in a unique position to recognize potentially dangerous activity along transportation routes and in public places. In addition, the inclusion of postal workers and utility workers make sense because they have been identified as targets for terrorism. Postal workers in New Jersey and Washington, DC, were earlier victims of anthrax terrorist attacks. As attacks on utility plants and water systems could affect the public health and safety of millions of people, these facilities have long been considered prime targets of domestic and international terrorism.

There are also existing programs, such as Highway Watch, River Watch, and Coast Watch, that could be expanded to include terrorist awareness. In the Coast Watch, maritime industries currently report all chemical, radiological, etiological, oil, and biological releases to the National Response Center, which has expertise in dealing with the release of hazardous materials and emergency situations. In the Highway Watch, professional truck drivers are trained to recognize and report a variety of incidents such as stranded motorists, drunk drivers, changing road conditions, accidents, etc. The River Watch engages the boating public and shoreline owners and operators to assist in protecting the borders from illegal entry into the country by undocumented aliens, drug smugglers, etc. Two of these groups proved invaluable when a domestic airliner emergency landed in the East River in 2009.

With regard to the employees and personnel,

1. Employers should be directed to verify the identity of all contractor's employees if an outside vendor has been hired to work in the plant.
2. Employers should perform background checks on all new employees.
3. Personnel who move freely throughout the plant should watch for signs of sabotage to equipment.
4. All bags that are brought into the plant should be checked by security personnel.

With regard to the nonemployees and visitors,

1. Movement of all nonemployees (deliveries, outside repair and maintenance, plant tours, etc.) should be restricted.

2. Visitors should be screened by having them show identification and sign in. The visitor roster should be maintained for 6–12 months. All visitors, including regulatory inspectors, should wear visitor passes when in the facility.

With regard to the within the plant itself:

1. Make sure that protective and security equipment, such as screens or metal detectors, are in place and functioning.
2. Keep entry doors and other entrances secure and locked where fire codes permit.
3. Maintain an inventory of all hazardous chemicals and review security and inventory procedures for this material on a regular basis. Are they stored in a nonsecure, nonsupervised area? Are they stored outside? Are bulk delivery systems secured? Is it easy for a disgruntled employee or terrorist to obtain chemicals and potentially add these to the production system?
4. For ingredient safety, know the suppliers and have an inspection system for incoming ingredients.

After all other safety precautions have been implemented, consider the following:

1. Invite local law enforcement agencies to review security measures.
2. If a telephone threat is received about a specific product, record or write down every word said. It is too risky to consider anything a practical joke.
3. Take precautions when handling mail that enters the facility. Mail handlers should use disposable gloves and be particularly aware of suspicious packages.

This case study should consider the armaments present in the facility. Discussions should center on the “equipment” unique to the Navy Yard.

19.4 Case Study 3: Plans to Counter the Possibility of a Process or Plant-Related Accident at the “Wedo” Chemical Facility in Suffolk County, Long Island, New York

Provide plans to counter a plant-related accident of the “Wedo” chemical plant in Suffolk County, Long Island, NY [3]. The plant is located on a 37 acre site and employs slightly more than 6000 workers.

Solution

The company policy statement regarding Health, Safety, and the Environment (HSE) is provided in the following:

The Wedo Chemical Company is committed to operations, products, and practices which protect safety, health and the environment. This commitment is to employees, contractors, neighbors, customers and all others affected by its operations. The company will be prepared for emergencies and will respond quickly, effectively, and with care to incidents or emergencies associated with the manufacture, transport, use, storage and disposal of its products. Each operating facility shall establish appropriate emergency response plans and capabilities as necessary to fulfill this commitment.

The plan for the Suffolk County plant must operate under this commitment. Wedo Chemical Company, hereafter referred to as the Company, has a strong commitment to the responsible management of their plants. The emergency management plan outlined in the following should be a strong indication of this plant site's commitment to these ideals. This program is not a one-time event. It is a total commitment to HSE excellence over a period of time.

The first entity created as part of this commitment will be a Site Operations Committee (SOC). They will meet weekly to discuss HSE topics. It will be chaired by the site manager and will include the following people: the plant manager, a human resources representative, a safety/environmental/risk manager, and the plant safety coordinator. The general discussion at these meetings will include:

1. A review of HSE incidents
2. Discussion by each member of HSE program issues in their area
3. Discussion by the group of HSE program concerns and suggestions
4. Review of safety efforts within plant teams

The committee will develop and maintain a realistic and credible plant-wide HSE policy.

The Operations Advisory Committee (OAC) will report directly to the SOC, will meet monthly to provide a realistic approach to implementing the necessary programs for addressing HSE-related issues, and has the final review on all HSE matters relating to plant operations. The main purpose of this committee is to integrate concerns and needs of the rank and file workers into the HSE program. This gives them ownership of the program and will make it easier for the members to "buy into" it. This committee will be cochaired by the plant manager and the union safety leader. The other members of this committee will be drawn from the maintenance section leaders,

union representatives, the plant safety coordinator, and other workers from the affected areas to be discussed. The role of this committee is defined as follows:

1. Serve as a communication link to/from workers at all levels of the workforce
2. Review, endorse, and modify programs to promote improvements in HSE matters throughout the plant
3. Develop new programs as needed
4. Jointly resolve safety issues
5. Communicate with and compliment other safety groups
6. Help to anticipate hazards and work with the business lines to resolve existing safety work issues and avoid new ones
7. Monitor and provide continuity for HSE standards in facilities and procedures, and monitor the progress in plant programs aimed at a more secure workplace

The mechanical operations team (MOT) will hold weekly meetings to discuss topics of interest as well as safety ideas and concerns of the team. The first line leader will serve as the team leader. Team leaders are responsible for coordinating the agendas and selecting HSE items which have arisen during the week for discussion by the group. The teams will be associated directly with the different sections in the plant. Issues that extend beyond that of a single team should be presented to other maintenance teams, including the mechanical group as a whole. This will sometimes require the creation of a coordination team to bring the separate teams together. This can be accomplished at departmental meetings. Members of the individual teams can present information of their activities and share plant-wide issues at these larger group meetings.

The mechanical department should utilize its regular meetings to collect all the information from the individual unit meetings, and it should perform follow-ups regarding concerns and issues brought to its attention by the individual teams.

Process meetings are conducted each week for members of both the shift and unit teams. This provides for continuous safety involvement during the off-hours and on a weekly basis between members of the specified unit.

The shift safety team consists of members of the unit shift teams. The shift team leader serves as a coordinator for these individual unit teams. Issues that surface during shift safety team meetings should be brought to the shift team leader's attention and should be included in the weekly meetings for discussion with the entire team. The shift team leader will coordinate all of these meetings. During day shifts, the unit team meetings are to be held by the unit leaders and first line leaders who will both

participate in the meetings, addressing unit specific concern and providing feedback to the unit team. The section leader can share unit issues, which are of interest to the overall group. This will help to communicate information to all personnel.

This commitment to HSE should extend to all workers in the plant. This means that a contractor safety team (CST) should be formed to address HSE issues faced by contractors and other third parties working at the plant. This committee will consist of the plant contract coordinators, contractors, and other members of the Company's other safety entities as needed. The project management leader will chair this team. The main purpose of this team will be to ensure that the same standards set for the companies' employees are communicated and reinforced with the contractor personnel. This committee will also play a role in the contractor selection process.

The "Wedo" plant's Rules and Procedures Committee will oversee the rules and procedures contained in the HSE manual, as well as those used and developed in other areas that may be specific to a particular operating unit. This committee will be made up of representatives of the operations, maintenance, industrial hygiene, and safety sections of the plant. Their duties will include:

1. Regular meetings to review rules and procedures to ensure that they are current and realistic
2. Meeting as needed to discuss/review new rules and procedures submitted or change requests to existing procedures
3. Review for the OAC all approved additions or changes for inclusion in the HSE manual
4. Obtain/develop resources for the communication of rules and procedures to employees

All of these committees will require support structures to perform their intended functions. The majority of this support will come from the safety, environmental, risk management coordinator and the industrial hygiene coordinator. These two coordinators will continuously implement new programs to reinforce the HSE commitment program. They will provide the committees with the following:

1. Training programs for management personnel to carry out HSE efforts
2. Information/topics for the team safety meetings
3. Tracking of incident performance for recognition of trends
4. Coordination of activities of the HSE commitment program
5. OSHA and EPA style audits of the programs and the plant

6. Personnel HSE issues relevant to the OAC
7. Management of the recognition of HSE milestones and achievements
8. Integration of HSE issues into other activities through various functions, i.e., making sure that everything done in the plant is considered from an HSE viewpoint

The objective of all of these support activities is to create a comprehensive HSE program that every member of the Company will follow. Each person will have the ability to have a direct impact on the safety of themselves and others around them. The Company's goal is to promote a total safety culture (TSC) within the plant. This requires attention to three basic factors:

1. *Environment*—tools, equipment, workplace, tasks
2. *Personnel*—attitudes, beliefs, and personalities
3. *Behavior*—safe and unsafe work practices, and intervention for others' safety

These factors are dynamic and interactive; influencing one factor will eventually have an impact on the other two. For example, changes in the environment have indirect effects on people's behaviors and attitudes, and behavior change usually results in some change in the environment. Therefore, a TSC must address each of these factors during the development and implementation of intervention strategies and throughout the ongoing evaluation and refinement of each process.

The following is a list of items that can help to promote a TSC within a company:

1. *Safety surveys*: performed while a person carries out their everyday work tasks with a focus on the person, behavior, and work environment
2. *Safety meetings*: good for bringing up concerns, addressing them, and providing responses to individual's concerns
3. *Accountability*: making everyone accountable for the safety of themselves and others
4. *Involvement*: necessary from the top down; management needs to take ownership of the safety program, and the committees are set up to directly involve people from everywhere in the Company
5. *Recognition*: shows that safety and commitment to safety will be rewarded

All of these programs together should provide for a work environment that is as safe as possible. The committees identified earlier will help to define an HSE program that will prevent accidents, promote employee moral, and

define what steps need to be taken in case of an accident. This program will provide the best return on the Company's investment of time and money because it will be specifically tailored to the needs and wants of this plant by the people that know the plant best—its workers and its management. An overall safety plan can be developed outside the plant, but it runs the risk of not being followed because it may have aspects that do not apply to the plant, or the workers may see it as an outside intervention when they believe they know what is best for the plant. These committees help to give the workers the ability to identify what is best for the plant while providing the highest level of safety possible.

This case study should consider the merits of the “Wedo” chemical plant's approach to emergency planning and response. Does the plan represent a bit of overkill? (*Hint*: consider the acreage of the plant and the number of employees). Are any modifications recommended that may lead to improving its effectiveness?

19.5 Case Study 4: Dilution Ventilation Models

Exposure to contaminants in a workplace can be reduced by proper ventilation [4–7]. Ventilation can be provided either by a *local exhaust* system or by *dilution ventilation*. In a local exhaust system, the contaminant itself is removed from the source through hoods. In dilution ventilation, air is brought into the work area to dilute the contaminant sufficiently to minimize its concentration and subsequently reduce worker exposure.

A local exhaust is generally preferred over a dilution ventilation system for health/hazard control because a local exhaust system removes the contaminants directly from the source, whereas dilution ventilation merely mixes the contaminant with uncontaminated air to reduce the contaminant concentration. Dilution ventilation may be acceptable when the contaminant concentration has a low toxicity and the rate of contaminant emission is constant and low enough that the quantity of required dilution air is not prohibitively large. However, dilution ventilation generally is not practical when the acceptable concentration of the contaminant is less than 100 ppm.

In determining the quantity of dilution air required, one must consider mixing characteristics of the work area in addition to the quantity (mass or volume) of contaminant to be diluted. Thus, the amount of air required in a dilution ventilation system is much higher than the amount required in a local exhaust system. In addition, if the replacement air requires heating or cooling to maintain an acceptable workplace temperature, then the operating cost of a dilution ventilation system may greatly exceed the cost of a local exhaust system.

The major components of any industrial ventilation system generally include the following:

1. Exhaust hoods
2. Ductwork
3. Contaminant control devices
4. Exhaust fans
5. Exhaust vents or stacks

Several types of hoods are available. One must select the appropriate hood for a specific operation to effectively remove contaminants from a work area and transport them into the ductwork. The ductwork must be sized such that the contaminant is transported without being deposited within the duct; adequate velocity must be maintained in the duct to accomplish this. Selecting a control device that is optimal for removal of the contaminant is important to ensure meeting relevant pollution control removal efficiency requirements. The exhaust fan is the workhorse of the ventilation system. The fan must provide the necessary volumetric flow at the required static pressure and must be capable of handling contaminated air characteristics such as dustiness, corrosiveness, and moisture in the air stream.

Properly venting the exhaust out of the building is often necessary to avoid contaminant recirculation into the air intake or into the building through other openings. Such problems can be minimized by properly locating the vent pipe in relation to the aerodynamic characteristics of the building. In addition, all or a portion of the cleaned air may be recirculated to the workplace. Primary (outside) air may be added to the workplace and is referred to as makeup air; the temperature and humidity of the makeup air may have to be controlled. It also may be necessary to exhaust a portion of the room air.

Your consulting firm has received a contract to develop, as part of an emergency planning and preparation plan, a mathematical model describing the concentration of a nanochemical in a medium-sized ventilated laboratory room. The following information (SI units) is provided:

V = volume of room, m^3

q = volumetric flow rate of ventilation air, m^3/min

c_{in} = concentration of the nanochemical coming into the ventilated room, gmol/m^3

c = concentration of the nanochemical leaving the ventilated room, gmol/m^3

c_o = concentration of the nanochemical initially present in ventilated room, gmol/m^3

r = rate of disappearance of the nanochemical in the room due to reaction and/or other effects, units depend on the reaction law assumed for the disappearance rate

As an authority in the field (having earlier taken a course on health, safety and accident management with the nefarious Dr. Theodore), you have been requested to:

1. Develop the equation describing the concentration in the room as a function of time if there are no "reaction" effects, that is, $r=0$.
2. Develop the equation describing the concentration in the room as a function of time if $r=-k$. Note that the minus sign indicates the chemical is disappearing.
3. Develop the equation describing the concentration in the room as a function of time if $r=-kc$. Note that the minus sign indicates the chemical is disappearing.
4. For Part 2, discuss the effect on the resultant equation if k is extremely small, that is, $k \rightarrow 0$.
5. For Part 3, discuss the effect on the resultant equation if k is extremely small, that is, $k \rightarrow 0$.
6. For Part 1, *qualitatively* discuss the effect on the final equation if the volumetric flow rate, q , varies sinusoidally.
7. For Part 1, *qualitatively* discuss the effect on the final equation if the inlet concentration, c_{in} , varies sinusoidally.

Assume the air in the laboratory is perfectly mixed.

Solution

Use the laboratory room as the control volume. Apply the law of conservation of mass to the nanochemical to develop the initial governing equation:

$$\begin{aligned} &\{\text{Rate of mass in}\} - \{\text{Rate of mass out}\} \\ &\quad \pm \{\text{Rate of mass generated or destroyed in the room}\} \\ &= \{\text{Rate of mass accumulated in the room}\} \end{aligned} \quad (19.1)$$

Employing the notation specified in the problem statement gives:

$$\{\text{Rate of mass in}\} = qc_{in} \quad (19.2)$$

$$\{\text{Rate of mass out}\} = qc \quad (19.3)$$

$$\{\text{Rate of mass generated}\} = rV \quad (19.4)$$

$$\{\text{Rate of mass accumulated}\} = V \frac{dc}{dt} \quad (19.5)$$

Substituting the previous equations gives:

$$qc_{in} - qc + rV = V \frac{dc}{dt} \quad (19.6)$$

Rearrangement leads to:

$$\frac{q}{V}(c_{in} - c) + r = \frac{dc}{dt} \quad (19.7)$$

The term V/q represents the average time the nanochemicals remain in the room, or their residence time, and is commonly designated as θ . Equation 19.7 may then be rewritten as:

$$\frac{dc}{dt} = \frac{c_{in} - c}{\theta} + r \quad (19.8)$$

1. If it is assumed that the nanoparticles do not react, $r = 0$. Substituting this into Equation 19.8 for r yields:

$$\frac{dc}{dt} = \frac{c_{in} - c}{\theta} + 0; \quad \frac{dc}{dt} = \frac{c_{in} - c}{\theta} \quad (19.9)$$

Separating variables and integrating yields:

$$\begin{aligned} \frac{dc}{c_{in} - c} &= \frac{dt}{\theta} \\ \int_{c_o}^c \frac{dc}{c_{in} - c} &= \int_0^t \frac{dt}{\theta} \\ -\ln\left(\frac{c_{in} - c}{c_{in} - c_o}\right) &= \frac{t}{\theta} \\ \left(\frac{c_{in} - c}{c_{in} - c_o}\right) &= e^{-t/\theta} \\ c &= c_{in} - (c_{in} - c_o)e^{-t/\theta} = c_{in} + (c_o - c_{in})e^{-t/\theta} \end{aligned} \quad (19.10)$$

2. If it is assumed that the nanoparticles react according to a zero-order rate law, $r = -k$. Substituting this into Equation 19.8 for r yields:

$$\frac{dc}{dt} = \frac{c_{in} - c}{\theta} - k = \frac{c_{in}}{\theta} - k - \frac{c}{\theta} = \left(\frac{c_{in} - k\theta}{\theta}\right) - \frac{c}{\theta} = (c_{in} - k\theta - c)\left(\frac{1}{\theta}\right) \quad (19.11)$$

Separating variables and integrating yields:

$$\begin{aligned}
 \frac{dc}{[(c_{in} - k\theta) - c]} &= \frac{dt}{\theta} \\
 \int_{c_o}^c \frac{dc}{[(c_{in} - k\theta) - c]} &= \int_0^t \frac{dt}{\theta} \\
 -\ln \left[\frac{(c_{in} - k\theta) - c}{(c_{in} - k\theta) - c_o} \right] &= \frac{dt}{\theta} \\
 \frac{(c_{in} - k\theta) - c}{(c_{in} - k\theta) - c_o} &= e^{-(t/\theta)} \\
 c &= c_o e^{-t/\theta} + (c_{in} - k\theta)(1 - e^{-t/\theta}) \quad (19.12)
 \end{aligned}$$

3. If it is assumed that the nanoparticles react according to a first-order rate law, $r = -kc$. Substituting this into Equation 19.8 for r yields:

$$\begin{aligned}
 \frac{dc}{dt} &= \frac{c_{in} - c}{\theta} - kc = \frac{c_{in}}{\theta} - \frac{c}{\theta} - kc = \frac{c_{in}}{\theta} - c \left(\frac{1 + k\theta}{\theta} \right) \\
 &= [c_{in} - (1 + k\theta)c] \left(\frac{1}{\theta} \right) \quad (19.13)
 \end{aligned}$$

Separating variables and integrating yields:

$$\begin{aligned}
 \frac{dc}{[c_{in} - (1 + k\theta)c]} &= \frac{dt}{\theta} \\
 \int_{c_o}^c \frac{dc}{[c_{in} - (1 + k\theta)c]} &= \int_0^t \frac{dt}{\theta} \\
 -\left(\frac{1}{1 + k\theta} \right) \ln \left[\frac{c_{in} - (1 + k\theta)c}{c_{in} - (1 + k\theta)c_o} \right] &= \frac{t}{\theta} \\
 \left(\frac{c_{in} - (1 + k\theta)c}{c_{in} - (1 + k\theta)c_o} \right) &= e^{-(t/\theta)(1 + k\theta)} \\
 c &= c_o e^{-t/\theta(1 + k\theta)} + \left(\frac{c_{in}}{1 + k\theta} \right) [1 - e^{-(t/\theta)(1 + k\theta)}] \quad (19.14)
 \end{aligned}$$

4. Using the solution to Part 2, the impact of assuming k is extremely small can be evaluated by setting $k=0$ in Equation 19.12 as follows:

$$\begin{aligned}
 c &= c_o e^{-t/\theta} + (c_{in} - k\theta)(1 - e^{-t/\theta}) = c_o e^{-t/\theta} + (c_{in} - c_{in} e^{-t/\theta}) \\
 &= c_{in} + (c_o - c_{in})e^{-t/\theta}
 \end{aligned}$$

It should be noted that this equation is identical to Equation 19.10, the equation derived from the mass balance expression assuming no reaction of the nanochemical.

5. Using the solution to Part 3, the impact of assuming k is extremely small can be evaluated by setting $k=0$ in Equation 19.14 as follows:

$$c = c_o e^{-(t/\theta)(1+0*\theta)} + \left(\frac{c_{in}}{1+0*\theta} \right) [1 - e^{-(t/\theta)(1+0*\theta)}] = c_o e^{-(t/\theta)} + c_{in} [1 - e^{-(t/\theta)}]$$

$$c = c_{in} + (c_o - c_{in})e^{-t/\theta}$$

Once again, it should be noted that this equation is identical to Equation 19.10, the equation derived from the mass balance expression assuming no reaction of the nanochemical.

6. Solving the mass balance equation becomes more complex if q varies with time, resulting in variable values of θ with time. These variations in the nanochemical residence time within the “reactor” need to be included in the original mass balance equation as:

$$\frac{dc}{dt} = \frac{c_{in} - c}{\theta} + r; \quad \theta = \theta(t) \quad (19.15)$$

Solving this form of the equation may require numerical methods.

7. As indicated in Part 6, if c_{in} is a function of t , the expression for c_{in} needs to be incorporated into the original mass balance equation for the problem, and the differential equation then needs to be solved using a table of integrals or a numerical method.

The discussion for this case study should center on demonstrating the usefulness of the equations developed earlier by using them in real-life applications. For example, consider the application of the aforementioned models to the following four applications [4,6,7]:

1. Calculate the minimum air ventilation flow rate containing 10 ng/m³ nanoparticles into the room to assure that the nanoagent concentration does not exceed 35.0 ng/m³. The nanoagents are appearing in the laboratory at a rate of 250 ng/min. Assume steady-state conditions.

2. Calculate the steady-state concentration in the laboratory that develops from an initial concentration of the nanochemical of 500 ng/m^3 . There is no additional source of nanoagents (none are generated) and the ventilation air is essentially pure, i.e., there is no background nanoagent concentration.
3. If the room volume is 142 m^3 , the flow rate of the 10 ng/m^3 concentration ventilation air is $12.1 \text{ m}^3/\text{min}$, and nanoparticles are being generated at a steady rate of 30 ng/min , calculate how long it would take for the concentration to reach 20.7 ng/m^3 . The initial concentration in the laboratory c_0 is 85 ng/m^3 .
4. Refer to Application 3. How long would it take to achieve a concentration of 13.65 ng/m^3 ? How long would it take to reach 12.2 ng/m^3 ?

Solution

1. The applicable model for this application is the basic mass balance equation (Equation 19.7):

$$\frac{q}{V}(c_{in} - c) + r = \frac{dc}{dt} \quad (19.7)$$

Under steady-state conditions, $dc/dt = 0$, so Equation 19.7 simplifies to:

$$\frac{q}{V}(c_{in} - c) + r = 0; \quad \frac{q}{V}(c_{in} - c) = -r; \quad q = \frac{-rV}{(c_{in} - c)} \quad (19.16)$$

Pertinent information from the problem statement includes the following:

$$rV = 205 \text{ ng/min}; \quad c_{in} = 10 \text{ ng/m}^3; \quad c = 35 \text{ ng/m}^3$$

Substituting these values into Equation 19.16 gives:

$$q = \frac{-rV}{(c_{in} - c)} = \frac{-205 \text{ ng/min}}{(10 - 35 \text{ ng/m}^3)} = \frac{-205 \text{ ng/min}}{-25 \text{ ng/m}^3} = 8.2 \text{ m}^3/\text{min}$$

2. The applicable model for this application is once again the basic mass balance equation (Equation 19.7):

$$\frac{q}{V}(c_{in} - c) + r = \frac{dc}{dt} \quad (19.7)$$

Under steady-state conditions, $dc/dt=0$, so Equation 19.7 simplifies to

$$\frac{q}{V}(c_{in} - c) + r = 0; \quad \frac{q}{V}(c_{in} - c) = -r; \quad c = \frac{rV}{q} + c_{in} \quad (19.17)$$

Pertinent information from the problem statement includes the following:

$$rV = 0 \text{ ng/min}; \quad c_{in} = 0 \text{ ng/m}^3; \quad c_o = 500 \text{ ng/m}^3$$

Substituting these values into Equation 19.17 gives, as expected, the diluted steady-state concentration of

$$c = \frac{0}{q} + 0 = 0 \text{ ng/m}^3$$

3. The applicable model for this application is Equation 19.12, i.e., the equation is solved for a reaction rate of the nanoparticles equal to a zero-order rate, $+k$, as follows: (*Note: the change in sign in Equation 19.18 compared to Equation 19.12 occurs since the value of the rate constant for this form of the mass balance equation is positive, i.e., nanoparticles are being produced in this room.*)

$$c = c_o e^{-t/\theta} + (c_{in} + k\theta)(1 - e^{-t/\theta}) \quad (19.18)$$

Pertinent information from the problem statement includes the following:

$$\theta = \frac{V}{q} = \frac{142 \text{ m}^3}{12.1 \text{ m}^3/\text{min}} = 11.74 \text{ min}$$

$$\begin{aligned} rV = kV = 30 \text{ ng/min}, \quad k &= \frac{30 \text{ ng/min}}{V} = + \frac{30 \text{ ng/min}}{142 \text{ m}^3} \\ &= +0.211 \text{ ng/m}^3\text{-min} \end{aligned}$$

$$c_{in} = 10 \text{ ng/m}^3; \quad c_o = 85 \text{ ng/m}^3; \quad c = 20.7 \text{ ng/m}^3$$

Substituting these values into Equation 19.18 gives:

$$\begin{aligned} 20.7 \text{ ng/m}^3 &= (85 \text{ ng/m}^3)e^{-t/11.74 \text{ min}} \\ &+ (10 \text{ ng/m}^3 + 0.211 \text{ ng/m}^3 \cdot \text{min}(11.74 \text{ min})) \\ &\times (1 - e^{-t/11.74 \text{ min}}) \end{aligned}$$

$$\begin{aligned} 20.7 \text{ ng/m}^3 &= (85 \text{ ng/m}^3)e^{-t/11.74 \text{ min}} \\ &+ (12.48 \text{ ng/m}^3) - (12.48 \text{ ng/m}^3)e^{-t/11.74 \text{ min}} \end{aligned}$$

This reduces to:

$$8.22 \text{ ng/m}^3 = (72.52 \text{ ng/m}^3)e^{-t/11.74 \text{ min}}; \quad 0.1133 \text{ ng/m}^3 = e^{-t/11.74 \text{ min}}$$

or solving for t :

$$\ln(0.1133) = -\frac{t}{11.74}$$

$$t = -\ln(0.1133)(11.74) = (2.18)(11.74) = 25.6 \text{ min}$$

4. The time to achieve a steady-state concentration of 13.65 ng/m^3 can be determined by substituting this new value of c into Equation 19.18 and simplifying to yield:

$$\begin{aligned} 13.65 \text{ ng/m}^3 &= (85 \text{ ng/m}^3)e^{-t/11.74 \text{ min}} \\ &+ (12.48 \text{ ng/m}^3) - (12.48 \text{ ng/m}^3)e^{-t/11.74 \text{ min}} \end{aligned}$$

$$1.17 \text{ ng/m}^3 = (72.52 \text{ ng/m}^3)e^{-t/11.74 \text{ min}}$$

$$0.0161 = e^{-t/11.74 \text{ min}}$$

or

$$\ln(0.0161) = \frac{-t}{11.74}$$

$$t = -\ln(0.0161)(11.74) = (4.13)(11.74) = 48.49 \text{ min}$$

The time to achieve a steady-state concentration of 12.2 ng/m^3 can be determined in a similar manner, by substituting this new value of c into Equation 19.18 and simplifying to yield:

$$\begin{aligned}
 12.2 \text{ ng/m}^3 &= (85 \text{ ng/m}^3)e^{-t/11.74 \text{ min}} \\
 &\quad + (12.48 \text{ ng/m}^3) - (12.48 \text{ ng/m}^3)e^{-t/11.74 \text{ min}} \\
 -0.28 \text{ ng/m}^3 &= (72.52 \text{ ng/m}^3)e^{-t/11.74 \text{ min}} \\
 -0.0039 &= e^{-t/11.74 \text{ min}} \\
 \ln(-0.0039) &= \frac{-t}{11.74}
 \end{aligned}$$

This cannot be solved, suggesting that with operating conditions as specified in the problem statement, this concentration cannot be reached no matter how long the room is ventilated. The steady-state concentration for this problem can be determined by setting the left-hand side of Equation 19.11 (with a $+k$ value for the zero-order rate of nanoparticle reaction) to zero and solving as follows:

$$\frac{dc}{dt} = 0 = \frac{c_{in} - c}{\theta} + k = \frac{c_{in}}{\theta} + k - \frac{c}{\theta} = \left(\frac{c_{in} + k\theta}{\theta} \right) - \frac{c}{\theta} = (c_{in} + k\theta - c) \left(\frac{1}{\theta} \right) \quad (19.19)$$

$$\begin{aligned}
 (c_{in} + k\theta - c) \left(\frac{1}{\theta} \right) &= 0 \\
 c &= c_{in} + k\theta \quad (19.20)
 \end{aligned}$$

Substituting the input values from the problem statement into Equation 19.20 yields a steady-state concentration for long ventilation times of:

$$c = 10 \text{ ng/m}^3 + (0.211 \text{ ng/m}^3 \cdot \text{min})(11.74 \text{ min}) = (10 + 2.48) = 12.48 \text{ ng/m}^3$$

This steady-state concentration represents the minimum concentration achievable in the laboratory based on the conditions specified. Therefore, the concentration can never reach a value of 12.2 ng/m^3 unless conditions are changed, i.e., a higher ventilation rate, a zero nanoparticle concentration in the ventilation air, etc.

This case study discussion can continue with nearly an infinite number of other relevant applications.

References

1. J. Ragona, adapted from Course 528—Accident and emergency management, Manhattan College, assignment submitted to L. Theodore, East Williston, NY, November 19, 2002.
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20

Natural Disasters

20.1 Introduction

A natural disaster is defined as a natural hazard, e.g., hurricane, flood, earthquake, etc., that affects the environment and leads to financial, environmental, and/or human losses. This introductory section serves as another review of the classes of natural disasters that have been experienced by mankind.

Natural disasters can generally be segregated into four disaster categories:

1. Land (avalanches, earthquakes, lahars—mudslides/landslides, volcanic eruptions)
2. Water (floods, limnic—gaseous lake emissions, tsunamis)
3. Weather (blizzards, hurricanes, or cyclonic storms, droughts, hailstorms, heat waves, tornadoes)
4. Space (gamma ray bursts, impact events—meteorites/asteroids, solar flares)

This chapter contains five case studies that focus on the hazards/risks associated with the following natural disasters:

Hurricanes

Floods

Earthquakes

Meteorites

Combined hurricanes and flooding

The application of statistical techniques to risk is emphasized in the material that follows.

20.2 Case Study 1: Hurricanes

“Hurricane” is the name applied to a class of disasters that usually originates over oceans in certain regions near the equator, and particularly to those storms arising in the Caribbean Sea and Gulf of Mexico.

Hurricanes have also been referred to as tropical cyclones, typhoons, cyclonic storms, and tropical depressions. They are characterized by high winds, torrential rain, high water waves, and tornadoes. These hurricanes develop over large water bodies, gradually fade out as they move inland, and are most commonly observed in late summer or early fall. A hurricane’s high winds circulate around a low-pressure center referred to as the eye of the storm. The low-pressure center develops when saturated warm air is forced upward by more dense, cooler air. Interestingly, hurricanes generally move in a path resembling the curve of a parabola. The atmospheric pressure drops sharply and the wind velocity rises from the outer edge of the storm toward its center. In a fully developed hurricane, the winds can attain velocities as high as 150 mph. The diameter of the area affected by winds of a destructive nature has exceeded 150 miles in some large storms. The winds cease abruptly within the eye of the storm, which averages approximately 15 miles in diameter. The seas are exceptionally violent during this period.

The paths of hurricanes have been well documented since the 1870s and their intensities have been estimated since the turn of the twentieth century. These data indicate that the average frequency of hurricanes striking the United States is slightly more than two per year; Florida experiences the highest at approximately one per year, and Texas is second at about one every 2 years.

Regarding the effect of hurricanes on industry, process equipment losses are generally infrequent. However, they can cause significant property and business-interruption problems as a result of flooding, wind pressures, and accompanying power failures. Hurricane warnings can be provided 2 or 3 days before landfall to allow for evacuations of susceptible populations, but evacuation is not a luxury that applies to coastal chemical plants and refineries, nor to offshore industrial facilities.

The Mehale Insurance Company (MIC) has hired you (a recent graduate) to *estimate* the annual hurricane fatality rate for the 2010–2015 period. In addition, MIC has requested you to prepare a short report that provides your answer along with explanatory details.

Solution

After a review of the literature [1], the young engineer obtained past hurricane fatality rate data as presented in Table 20.1 and realizes that one of the statistical techniques that may be used to solve this problem is to regress the data in Table 20.1 and extrapolate the model generated to estimate the

TABLE 20.1
Fatality Rate/Property Loss Data for Case Study 1

10 Year Interval	Median Year	Fatality Rate (per Hurricane)	Property Loss (per Hurricane) × 10 ⁻⁶ (\$)
1920–1930	1925	118	83
1930–1940	1935	55	210
1940–1950	1945	8	150
1950–1960	1955	33	456
1960–1970	1965	30	825
1970–1980	1975	19	1417
1980–1990	1985	9	676
1990–2000 ^a	1995	7	2103
2000–2010	2005	^b	^b
2010–2020	2015	—	—

^a Estimated.
^b Not available.

required information for future dates. The procedures and details to accomplish this task that were included in the final report follow [2].

Engineers and scientists often encounter applications that require the need to develop a mathematical relationship between data for two or more variables. For example, if Y (a dependent variable) is a function of or depends on X (an independent variable), i.e.,

$$Y = f(X)$$

(20.1)

one may be required to express these (X,Y) data in equation form. This process is referred to as *regression analysis*, and the regression method most often employed is the method of *least squares*.

An important step in this procedure—which is often omitted—is to prepare a plot of Y versus X to explore the nature of the relationship between these two variables. The result, referred to as a *scatter diagram*, could take on any form. Three such plots are provided in Figure 20.1a through c.

The first plot (a) suggests a linear relationship between X and Y , i.e.,

$$Y = a_0 + a_1X$$

(20.2)

The second graph (b) appears to be best represented by a second-order (or parabolic) relationship, i.e.,

$$Y = a_0 + a_1X + a_2X^2$$

(20.3)

The third plot (c) suggests a linear model that applies over two different ranges, i.e., it should represent the data using two linear relationships:

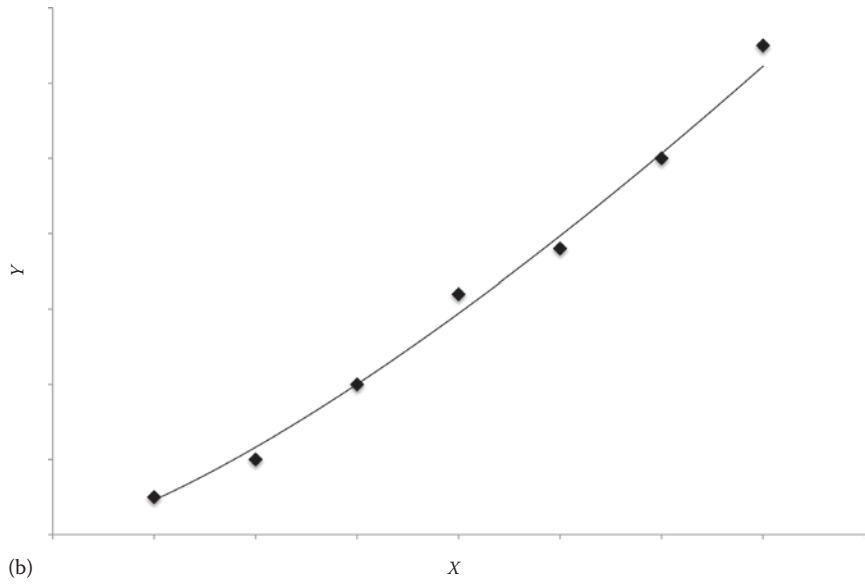
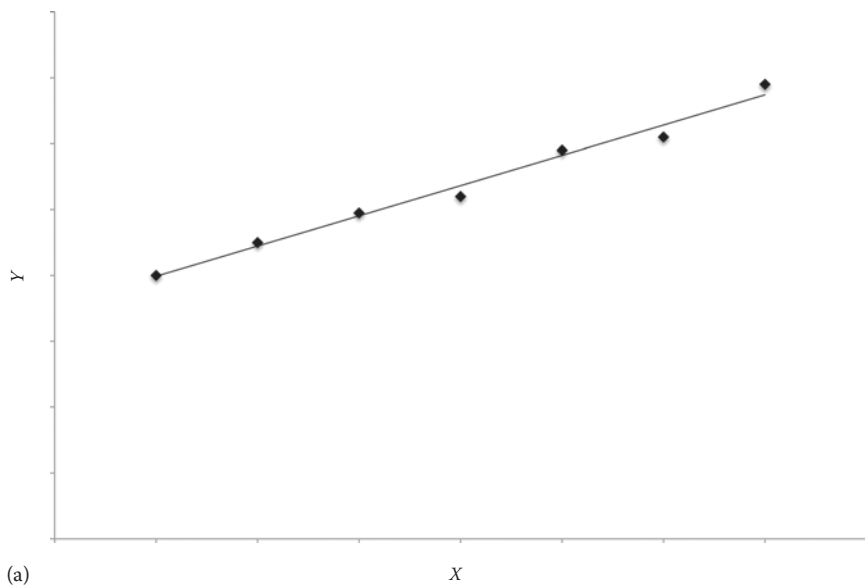


FIGURE 20.1
Scatter diagrams: (a) linear relationship, (b) parabolic relationship, and (c) dual-linear relationship.

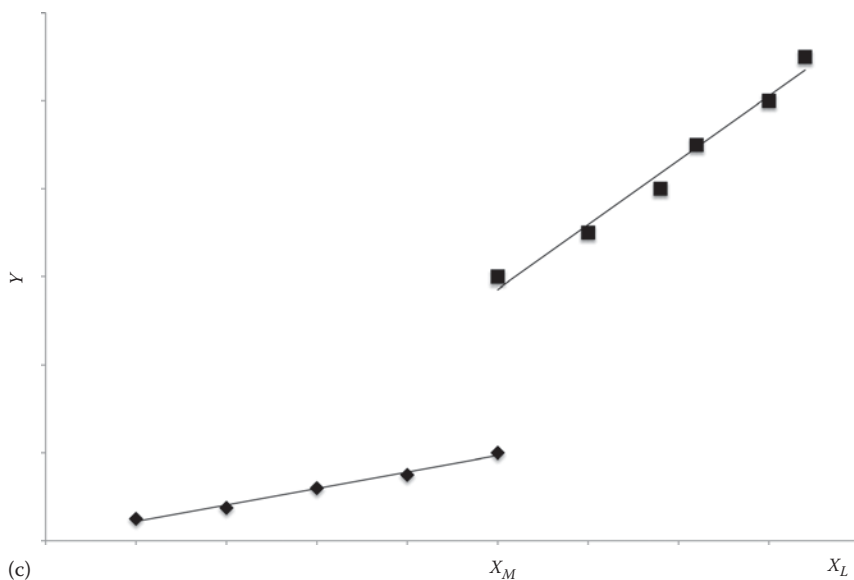


FIGURE 20.1 (continued)

$$Y = a_0 + a_1X; \quad X_0 < X < X_M \quad (20.4)$$

and

$$Y = a'_0 + a'_1X; \quad X_M < X < X_L \quad (20.5)$$

This multiequation model finds application in representing not only some risk applications but also adsorption equilibria, multiparticle size distributions, quantum energy relationships, etc. It is good practice, then, that a scatter diagram be generated and the plot be reviewed to suggest an appropriate model to be implemented at an early stage in the analysis.

In addition to the linear model (Equation 20.2) and the parabolic model (Equation 20.3) presented earlier, some of the other models often employed to develop regression relationships for technical data include the following:

$$\text{Cubic model: } Y = a_0 + a_1X + a_2X^2 + a_3X^3 \quad (20.6)$$

$$\text{Quadratic model: } Y = a_0 + a_1X + a_2X^2 + a_3X^3 + a_4X^4 \quad (20.7)$$

Procedures to evaluate the regression coefficients a_0 , a_1 , a_2 , etc., are provided later. The reader should note as indicated earlier that the analysis is based

on the method of least squares. This technique provides numerical values for the regression coefficients a_i , such that the sum of the squares of the difference (error) between the actual Y and the Y value predicted by the model equation is minimized. This is shown in Figure 20.2.

In Figure 20.2, the dots and triangles represent the measured (Y) and predicted (Y_e) values of the variable, respectively. On examining the two figures, one can immediately conclude that the error ($Y - Y_e$) squared and summed for the four points is less for the lower plot. Also note that a dashed line represents the error. The line that ultimately produces a minimum sum of the individual squared errors, that is, has its smallest possible value, is the regression model (based on the method of least squares). The proof is left as an exercise.

To evaluate a_0 and a_1 for a linear model (Equation 20.2), one employs the following least squares algorithm for n data points of Y and X :

$$a_0 n + a_1 \sum X = \sum Y \quad (20.8)$$

$$a_0 \sum X + a_1 \sum X^2 = \sum XY \quad (20.9)$$

All the quantities given, except a_0 and a_1 , can be easily calculated from the data. Because there are two equations and two unknowns, the set of equations can be solved for a_0 and a_1 . For this case,

$$a_1 = \frac{n \sum XY - \sum X \sum Y}{n \sum X^2 - \left(\sum X \right)^2} \quad (20.10)$$

Dividing numerator and denominator by n and defining $\bar{X} = \sum X/n$ and $\bar{Y} = \sum Y/n$ leads to:

$$a_1 = \frac{\sum XY - \left(\sum X \sum Y / n \right)}{\sum X^2 - \left(\sum X \right)^2 / n} = \frac{\sum XY - n \bar{X} \bar{Y}}{\sum X^2 - n \bar{X}^2} \quad (20.11)$$

Using this value of a_1 produces the following equation for a_0 :

$$a_0 = \bar{Y} - a_1 \bar{X} \quad (20.12)$$

If the model (or regression line) is forced to fit through the origin, then the calculated value of $Y_e = 0$ at $X = 0$. For this case, the regression line takes the form:

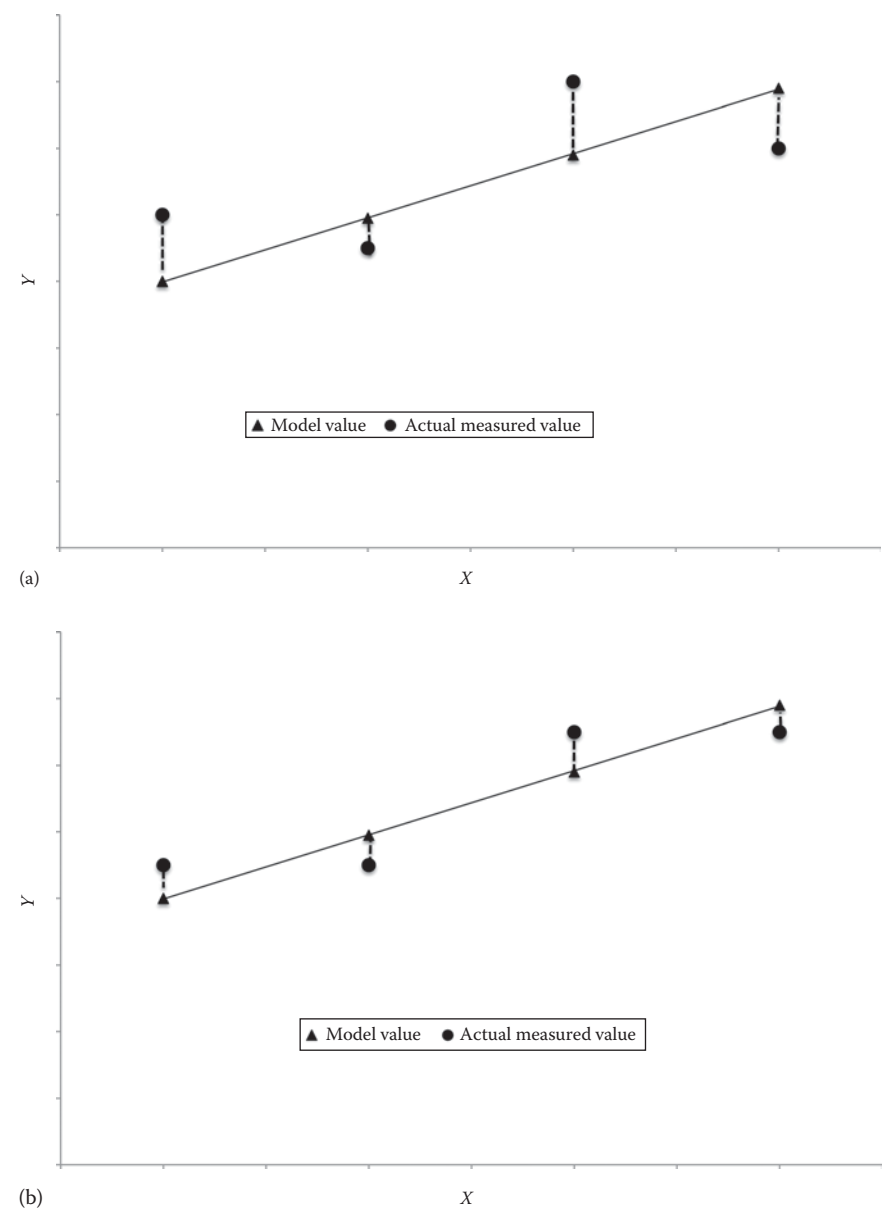


FIGURE 20.2
Error difference: actual and predicted values for (a) large least squares error and (b) small least squares error.

$$Y_e = a_1X; a_0 = 0 \quad (20.13)$$

with:

$$a_1 = \frac{\sum XY}{\sum X^2} \quad (20.14)$$

A cubic model takes the form (see Equation 20.6)

$$Y = a_0 + a_1X + a_2X^2 + a_3X^3 \quad (20.6)$$

For n pairs of X , Y values, the constants a_0 , a_1 , a_2 , and a_3 can also be obtained by the method of least squares so that $\Sigma(Y - Y_e)^2$ again has the smallest possible value, i.e., is minimized. The coefficients a_0 , a_1 , a_2 , and a_3 are the solution of the following system of four linear equations:

$$a_0n + a_1 \sum X + a_2 \sum X^2 + a_3 \sum X^3 = \sum Y \quad (20.15)$$

$$a_0 \sum X + a_1 \sum X^2 + a_2 \sum X^3 + a_3 \sum X^4 = \sum XY \quad (20.16)$$

$$a_0 \sum X^2 + a_1 \sum X^3 + a_2 \sum X^4 + a_3 \sum X^5 = \sum X^2Y \quad (20.17)$$

$$a_0 \sum X^3 + a_1 \sum X^4 + a_2 \sum X^5 + a_3 \sum X^6 = \sum X^3Y \quad (20.18)$$

Because there are four equations and four unknowns, this set of equations can be solved for a_0 , a_1 , a_2 , and a_3 . This development can be extended to other regression equations, e.g., exponential, hyperbola, higher order models, etc.

The correlation coefficient provides information on how well the model, or regression equation, fits the data. It is denoted by r and is given by:

$$r = \frac{\sum XY - (\sum X \sum Y)/n}{\sqrt{\left[\sum X^2 - (\sum X)^2/n\right] \left[\sum Y^2 - (\sum Y)^2/n\right]}} \quad (20.19)$$

or

$$r = \frac{n \sum XY - \sum X \sum Y}{\sqrt{n \left[\sum X^2 - \left(\sum X \right)^2 \right] \left[\sum Y^2 - \left(\sum Y \right)^2 \right]}} \quad (20.20)$$

or

$$r = \frac{\sum XY - n \bar{X} \bar{Y}}{\sqrt{\left(\sum X^2 - n \bar{X}^2 \right) \left(\sum Y^2 - n \bar{Y}^2 \right)}} \quad (20.21)$$

This equation can also be shown to take the form

$$r = \pm \left[\frac{\sum (\bar{Y} - Y_e)^2}{\sum (Y - \bar{Y})^2} \right]^{0.5} \quad (20.22)$$

The correlation coefficient satisfies the following six properties:

1. If all points of a scatter diagram lie on a line, then $r = +1$ or -1 . In addition, $r^2 = 1$. The square of the correlation coefficient is defined as the coefficient of determination.
2. If no linear relationship exists between the X s and Y s, then $r = 0$. Furthermore, $r^2 = 0$. It can be concluded that r is always between -1 and $+1$, and r^2 is always between 0 and 1 .
3. Values of r close to $+1$ or -1 are indicative of a strong linear relationship.
4. Values of r close to 0 are indicative of a weak linear relationship or one that is not linear between variables.
5. The correlation coefficient is positive or negative depending on whether the linear relationship has a positive or negative slope. Thus, positive values of r indicate that Y increases as X increases; negative values indicate that Y decreases as X increases.
6. If $r = 0$, it only indicates the lack of a linear correlation; X and Y might be strongly correlated by some nonlinear relation, as discussed earlier. Thus, r can only measure the strength of linear correlations; if the data are nonlinear, one should transform the data to attempt to linearize before computing r .

It should also be noted that the correlation coefficient only provides information on how well the model fits the data. It is emphasized that

r provides no information on how good the model is or, to reword this, whether this is the correct or best model to describe the functional relationship of the data.

After examining a plot of the data in Table 20.1, the young engineer decided to take the log transform of the annual fatality rate from 1920 through 2000, plot these transformed data versus the median year and employ a linear model to represent the data. The resulting regression equation of $\log(\text{fatality rate}, F)$ versus median year, M , is shown in Figure 20.3, and the regression relationship is given by:

$$\log(F) = 28.024 - 0.0136M \tag{20.23}$$

with $r=0.7636$.

The fatality rate for the year 2015 can be obtained by substituting this median year value directly into Equation 20.23 and calculating F as follows:

$$\log(F) = 28.024 - 0.0136(2015) = 28.024 - 27.404 = 0.62$$

$$F = 10^{0.62} = 4.17, \text{ or between 4 and 5 deaths/hurricane}$$

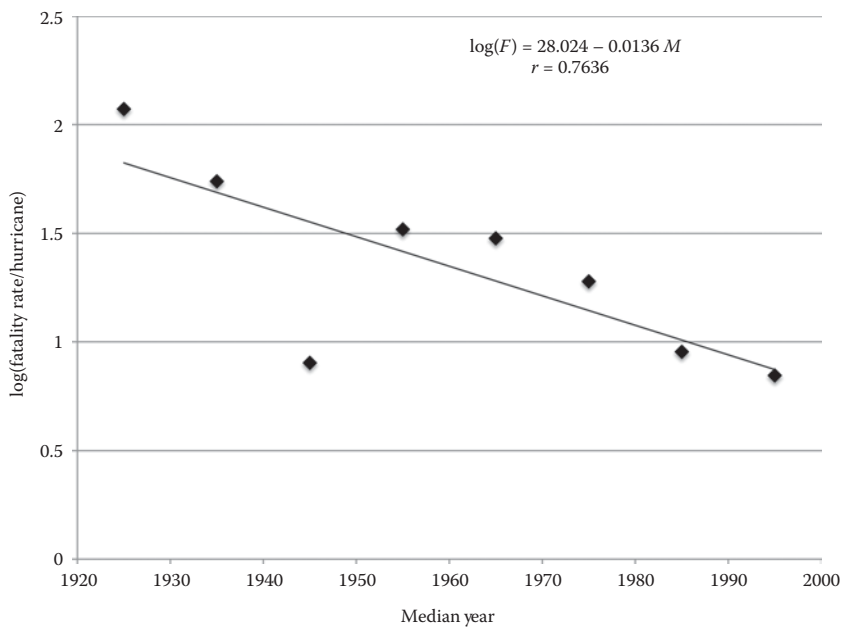


FIGURE 20.3 Scatterplot of $\log(\text{annual fatality rate})$ versus median year from historical hurricane fatality data for Case Study 1.

Any discussion of this case study should center on the validity of the statistical technique employed to solve the problem, and alternative solutions that might also provide a defensible solution to the problem.

20.3 Case Study 2: Floods

In a very general sense, a flood may be defined as an increase of flow of water that submerges land. Floods occur when soil becomes saturated from excessive rain and/or snow melt. The excess then “runs off” the land in quantities that cannot be handled by stream channels and/or reservoirs. *River floods* result from excessive rain, sometimes combined with melting snow, causing the rivers to overflow their banks. A flood that rises and falls rapidly with little to no warning is called a *flash flood* and usually results from intense rainfall over a relatively small area. Coastal areas can also be flooded by unusually high tides induced by high winds over the ocean and (in rare instances) by tidal waves caused by undersea earthquakes (tsunamis).

Negative effects of floods can include the following:

1. Soil erosion as well as sediment deposition problems downstream
2. Inundated property and loss of life
3. Interference with the economic use of lands
4. Severe damage to bridge abutments, sewer outfalls, and other infrastructure within floodways
5. Impairment to navigation and hydroelectric power production
6. Contamination of water and accompanying disease outbreaks
7. Failed crops

The three deadliest floods in recorded history occurred in China in 1887, 1931, and 1938 where it is estimated that approximately one million, three million, and one-half million people died, respectively. As noted in Chapter 3, the Indonesia tsunami of 2004 resulted in approximately 250,000 deaths. Positive effects of flooding include the following:

1. Recharge of groundwater
2. Improving soil fertility by providing nutrients in which it is deficient
3. Providing additional water resources in arid regions
4. Maintaining ecosystems in river corridors
5. Maintaining floodplain biodiversity

The basic methods of flood control have been practiced since early times. These methods include reforestation and the construction of levees, dams,

and reservoirs. Despite the fact that these controls have been known to fail catastrophically, people have lived and worked at or near water to capitalize on cheap and easy travel and commerce. In addition, and despite the threat of flooding, the economic and aesthetic value of living near water has usually exceeded the concerns of flooding for many.

A large metropolitan area in the southwest has decided to implement a series of levees (an embankment built alongside a waterway to prevent flooding by the river or sea) to reduce the probability of another flooding disaster in the future. An initial economic study performed by Ricci and Theodore (RAT) engineers, based on the height in inches, H , that the levees will fail and will adversely affect income from various recreational and tourist activities, produced the following results:

1. The total annualized net income (total income – losses due to property damage, loss of revenues, etc., due to flooding), AI , in units of $\$10^6/\text{year}$, is

$$AI = 10(H - 100) \quad (20.24)$$

2. The annualized cost (AC) in units of $\$10^6/\text{year}$, associated with the cost to design, install, and maintain the levees of height H is

$$AC = \frac{100,000}{(500 - H)} \quad (20.25)$$

RAT has further indicated that the aforementioned models apply for H in the 125–475 in. range.

Based on the initial analysis of RAT, estimate what height of the levees would result in the optimum profit P from the city's perspective. In effect, the process reduces to selecting a levee height that will maximize the difference between the AI and AC , that is, select H to maximize:

$$P = AI - AC \quad (20.26)$$

Solution

Since there are two contributing factors to the cost–profit model, one may substitute Equations 20.24 and 20.25 into Equation 20.26 to yield the following equation for the profit as a function of levee height:

$$P = 10(H - 100) - \frac{100,000}{(500 - H)} \quad (20.27)$$

To maximize (or minimize) the profit, the first derivative of P (Equation 20.27) with respect to H is set equal to zero, i.e.,

$$\frac{dP}{dH} = 10 - \frac{100,000}{(500 - H)^2} = 0 \quad (20.28)$$

Solving:

$$(500 - H)^2 = \frac{100,000}{10} = 10,000$$

$$500 - H = \pm\sqrt{10,000} = \pm 100$$

$$H = 500 \pm 100 = 400 \text{ in.}, 600 \text{ in.}$$

However, based on the physical interpretation of these roots, it is readily apparent that the levee height, H , cannot be greater than 475 in. Hence, the root $H=600$ in. has no physical meaning and may be neglected.

In order to determine if this root is the relative maxima, the *first derivative test* must be employed. By qualitatively examining the value of the derivative (\pm) on both sides of each root, an inference can be made as to whether the original function contained a relative maxima or a relative minima at the root. For instance, if the value of the profit changes in sign from positive to negative as the levee height is increased at the root, the slope of the line tangent to the original function changes from positive to negative at this point, and hence the root is a relative maxima in the original function (this assumes continuity about the point of interest in the original function). Inversely, should the sign change from negative to positive in the derivative, then the original function realizes a relative minima at the root. In this particular example, the values of the derivative arbitrarily close to the 400 in. levee height root have the values shown in Figure 20.4. A relative maxima in the *profit equation*, $P(H)$, is realized at $H=400$ in. Thus, for maximum profit, the levee height should equal to 400 in. Alternatively, the *second derivative test* may be employed, which examines a function's change about its point(s) of inflection. This test would yield the same result [3].

One may also extend this calculation to determine the value(s) of H that will lead to "breakeven" operation. For a breakeven operation, P is set equal to 0 in Equation 20.27 and the terms are rearranged so that:

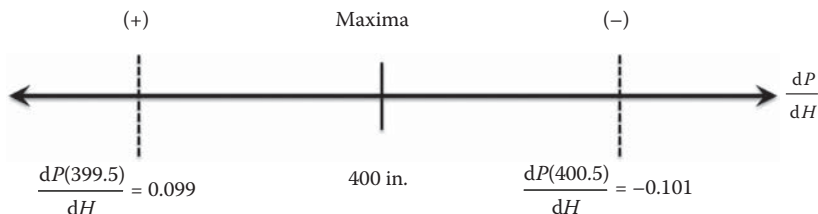


FIGURE 20.4

First derivative test for Case Study 2.

$$(500 - H)(H - 100) = \frac{10,000}{10} = 10,000$$

$$(H - 500)(H - 100) = -10,000$$

This may be expanded and rewritten as:

$$H^2 - (500 + 100)H + [(10,000) + (500)(100)] = 0$$

$$H^2 - 600H + (60,000) = 0$$

The solution to this quadratic equation is:

$$H = \frac{-(-600) \pm \sqrt{(-600)^2 - (4)(1)(60,000)}}{2(1)} = \frac{600 \pm 346.4}{2}$$

The two solutions for breakeven operation are:

$$H = 473.2 \text{ in.}, 126.8 \text{ in.}$$

Both values are within the feasible levee height limitations defined in the problem statement. What this result suggests is that a minimum levee height of 127 in. should be implemented, with profit increasing until a levee height of 400 in., beyond which profit decrease to a breakeven value at 473.2 in. Beyond 473.2 in., a higher levee costs more than the net income that it generates and should be the limit of levee height so that excess costs are not incurred by the city.

The reader should discuss how the problem would be solved with other information. The Katrina episode discussed in Chapter 3 could also be expanded through this case study.

20.4 Case Study 3: Earthquakes

An earthquake has also been referred to a quake, tremor, or as seismic activity. An earthquake produces vibrations at or near the Earth's surface when rocks, in which elastic strain has increased, suddenly rupture and then rebound. The resulting vibrations can range from being unnoticed to resulting in catastrophic destruction. The earthquake's point of initial rupture is defined as its *hypocenter* (or focus), while the term *epicenter* refers to the location at

ground level above the hypocenter. The magnitude of an earthquake is usually reported using the Richter scale. The Richter scale is based on a logarithmic relationship that varies from 1 to 10. For example, a magnitude 8 quake is 10 times more powerful than a magnitude 7 quake, 100 times more powerful than a magnitude 6 quake, 1000 times more powerful 5 quake, etc. Nearly 1000 quakes of magnitude 5–6 occur annually compared to 50,000 quakes of magnitude 3–4. Approximately one earthquake of magnitude 8–9 occurs annually.

Earthquakes with a Richter magnitude of 3 or lower are essentially imperceptible, while a magnitude of 7 can cause severe damage over large areas. Approximately 500,000 earthquakes occur each year, most of which cannot be detected by other than the most sensitive seismic equipment. It should be noted that minor earthquakes occur nearly constantly around the world. The largest earthquake that has been measured was of magnitude 9.5 in Chile in 1960.

Many earthquakes are accompanied by one or more *aftershocks*. An aftershock is defined as an earthquake that occurs after the main earthquake. The aftershock is in the same general region as the main shock but always of a smaller magnitude. Aftershocks occur as the crust around the displaced earth adjusts to the effects of the main shock.

The general subject of earthquakes has received attention since early times. Some of the ancient Greek philosophers attributed quakes to vapors in the cavities of the Earth, and winds and fires in the depths of the Earth. Others attributed them to tensions between the Earth and water, episodes of dryness and wetness, and underground thunderstorms.

The consequences of earthquakes include:

1. Ground shaking
2. Ground rupture
3. Landslides
4. Avalanches
5. Tsunamis
6. Floods
7. Excessive tidal forces

Because of these consequences and the risks associated with this natural phenomenon, research is actively being pursued to enable the prediction of when and where earthquakes will occur. The Chinese predicted a magnitude 7.3 earthquake in Haicheng in 1975, and nearly 100,000 residents were evacuated 2 days before the quake destroyed or damaged 90% of the buildings in the vicinity of the epicenter. One of the reported clues that led to this prediction was a chain of low-magnitude tremors, defined as *foreshocks*. Other predictions have been based on the tilting or bulging of the land surface, changes in the Earth's magnetic field, changes in the water levels of wells,

and in unusual animal behavior prior to a quake. The building of stress in the crust of the Earth is also being investigated as a means of predicting imminent earthquake activity.

A large metropolitan area located along the western coast of the United States has commissioned a study to determine, on *average*, the *annual* property loss that could arise due to an earthquake (plus secondary aftershocks) located at the center of the city (note that this represents a worst-case scenario).

The urban planners have the following information available. Doyle Geology Consultants have determined that for this city, the difference between the magnitude of a large earthquake as measured on the Richter scale and the earthquake threshold value of 3.25, which does not produce significant damage, is a random variable x having the (annual) probability distribution function [2]:

$$f(x) = 1.7e^{-1.7x}; x > 0; f(x) = 0; \text{ elsewhere} \quad (20.29)$$

The principal area of concern for the city fathers is with values of x ranging from 2 to 6 or earthquakes from 5.25 to 9.25 on the Richter scale. For example, applying the definition of this cumulative distribution function [2], substituting and integrating leads to:

$$P(2 < x < 6) = \int_2^6 1.7e^{-1.7x} dx = e^{-3.4} - e^{-10.2} = 0.0334 - 0.0 = 0.0334/\text{year}$$

Thus, the city can expect (on average) an earthquake in the magnitude 5.25–9.25 range at a frequency of 0.0334/year or occurring approximately once every 30 years.

Using the information provided above, the “city fathers” have decided to check on proposed annual insurance costs by determining the “expected” annual losses they are insuring against. The procedure recommended for this calculation follows.

The term $g(x)$ represents the approximate property loss occurring as a function of the Richter number with units of \$/occurrence. Doyle Geology suggests that for this analysis,

$$g(x) = 10^{[6+(x/3)]} \quad (20.30)$$

Solution

Assuming the aforementioned Richter number is constrained by 2.0 (lower end) and 6.0 (high end), the average annual loss (AL) to be expected is given by

$$AL = \frac{\int_{2.0}^{6.0} f(x)g(x)dx}{\int_{2.0}^{6.0} dx} = \frac{\int_{2.0}^{6.0} f(x)g(x)dx}{4} = \frac{\int_{2.0}^{6.0} I dx}{4} \quad (20.31)$$

where I is the integrand $f(x)g(x)$. Substituting the two functional relationships provided earlier (Equations 20.29 and 20.30) into Equation 20.31 leads to

$$AL = \frac{1}{4} \int_{2.0}^{6.0} \{(1.7e^{-1.7x})(10^{[6+(x/3)]})\}dx \quad (20.32)$$

This complex integral may be evaluated by any one of several methods. The authors chose to plot I from $x=2$ to 6 and obtain the area under the curve. This plot of Equation 20.32 is shown in Figure 20.5. The area under the curve is \$276,431/year, the estimated annual expected losses associated with damage occurring from earthquakes between 5.25 and 9.25 on the Richter scale.

The discussion of this case study should center on the validity of the models and/or the potential use of safety factors in estimating both the frequency of earthquake occurrences, as well as expected property loss when they do occur.

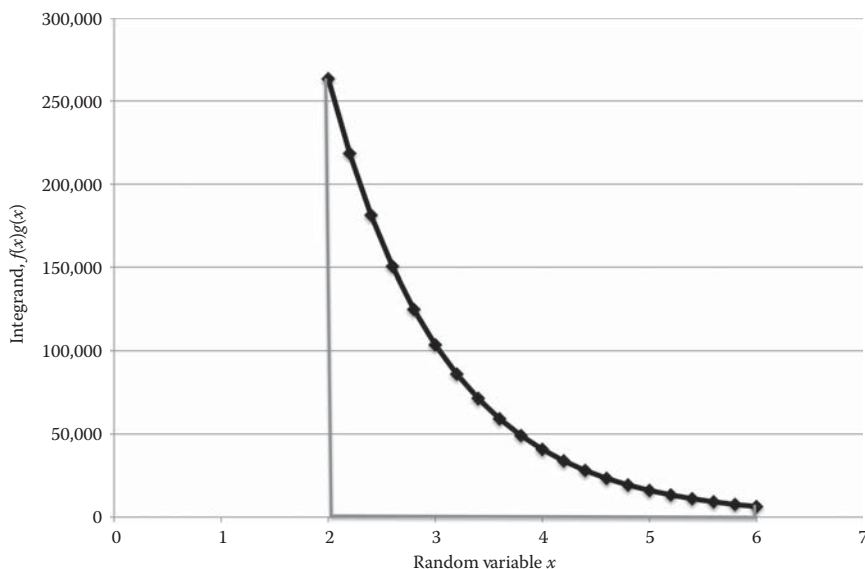


FIGURE 20.5

Plot of integrand, I , as a function of x for Case Study 3.

20.5 Case Study 4: Meteorites

A *meteor* is defined as a small solid body entering the Earth’s atmosphere from outer space. A meteor that reaches the Earth’s surface before it is completely consumed is defined as a *meteorite*. Some refer to large meteors/meteorites as *asteroids*, while others refer to asteroids as small planets. Meteorites can be large or small. Most are produced by impacts of larger asteroids. When meteorites enter the atmosphere, frictional forces cause the body to heat up and emit light, thus forming a fireball, also known as a *shooting star* or *falling star*. Finally, meteorites are almost always named for the place where they land, for example, Tunguska (Siberia).

Most meteors disintegrate on entering the atmosphere and typically arrive at the surface at their terminal settling velocity [3]. The impact normally creates a small pit. However, falling meteorites have been known to cause damage to property, animals, and people. Few meteorites are large enough to create large impact craters.

A large meteorite (hereafter referred to as an asteroid) is headed precariously close to the Earth’s orbit at an unprecedented velocity. By the time the asteroid will be closest to the Earth (based on the asteroid’s current trajectory), its orientation relative to the Earth will be as shown in Figure 20.6. (Note that the asteroid is traveling perpendicular to the plane

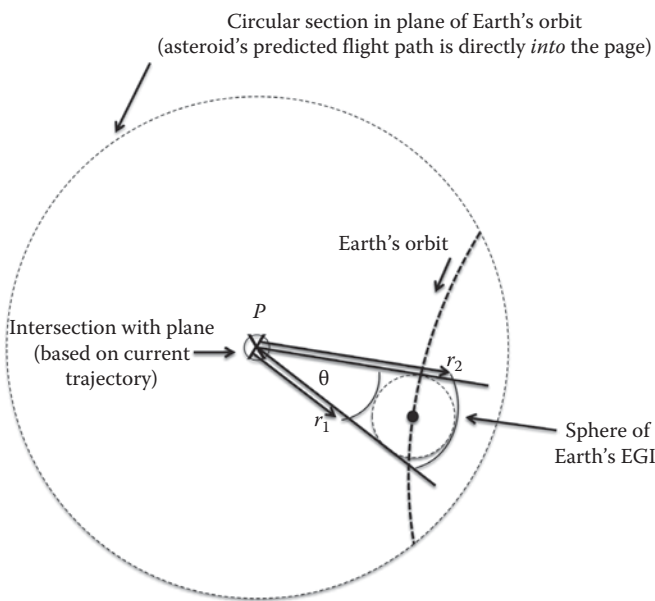


FIGURE 20.6
Projected location of asteroid relative to earth (not to scale) for Case Study 4.

of the Earth's orbit.) Should an unforeseen force, for example, a collision with a smaller asteroid, cause the asteroid to shift off course, the certainty of where it will cross the plane of the Earth's orbit decreases radially from the predicted point of intersection.

Because of the imminence of this event, a NASA physicist has hired Ricci Associates (RA) to develop a joint probability distribution function (JPDF) that describes the likelihood of where the asteroid will cross the plane of the Earth's orbit. The JPDF prepared by RA is shown in Figure 20.7 and given by Equation 20.33:

$$P(r, \theta) = \frac{\beta}{2\pi} \int_0^{\theta} \int_{r_1}^{r_2} \exp(-\beta r) dr d\theta \quad (20.33)$$

where

β is the model parameter = 5×10^{-5} miles $^{-1}$

r is the radial distance from the *projected* crossing point in the plane Earth's orbit ($r=0$), miles

θ is the central angle encompassing area of interest in the plane, rad

RA has also determined that the radius of the Earth's effective gravitational influence (EGI) for an asteroid of this mass is 4×10^5 miles (roughly

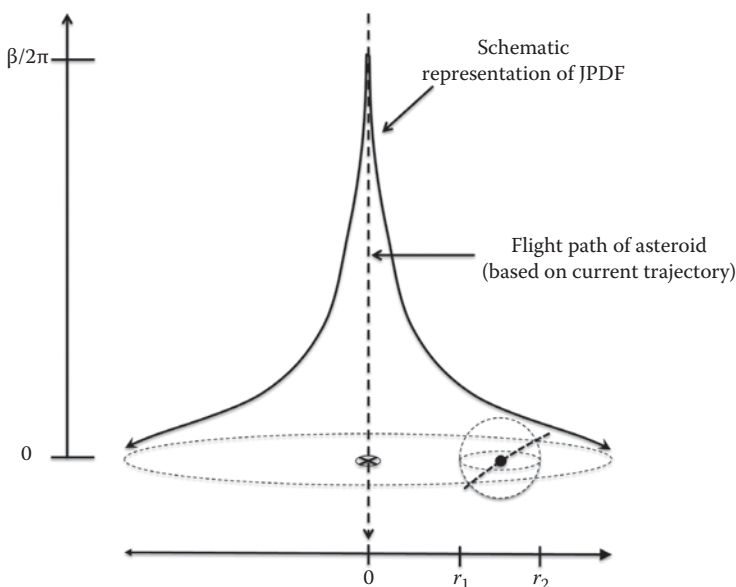


FIGURE 20.7

Joint probability distribution function (not to scale) for Case Study 4.

twice the average lunar distance from Earth). Based on the current flight path the asteroid will cross the plane of Earth's orbit at approximately 1×10^6 miles from the Earth's EGI, i.e., $r_1 = 1 \times 10^6$ miles. What is the probability that the asteroid's flight will deviate such that it *enters* the Earth's EGI? Assume that the asteroid is moving very fast relative to Earth's orbit [4].

Solution

A word of explanations of Equation 20.33 is in order before proceeding to the solution of the problem. The physical interpretation of $P(r, \theta)$ is as follows. Refer to Figure 20.7. Set V equal to the volume generated by revolving the area within the solid line(s) a total of 360° . Set E equal to the volume under the JPDE between r_1 and r_2 . Then,

$$P(r, q) = \frac{E}{V} \quad (20.34)$$

represents the probability that the asteroid will enter the EGI between r_1 and r_2 and thus strike Earth. If r_1 is 1×10^6 miles, then r_2 is simply calculated as r_1 plus the diameter of the sphere of EGI. Thus,

$$r_2 = r_1 + d_{EGI} = (1 \times 10^6) + 2(4 \times 10^5) = 1.8 \times 10^6 \text{ miles} \quad (20.35)$$

Since the asteroid is moving very quickly relative to the Earth, one need not be concerned with any changes in the Earth's position in the event that the asteroid changes course. In effect, the Earth is moving so slowly that its position in Figure 20.6 will be the same regardless of exactly where the asteroid crosses the plane of Earth's orbit. Hence, the probability as given by the JPDE may be applied once the angle, θ , has been determined. The angle may be calculated from the well-known geometric equation for a circle of radius r :

$$s = r\theta \quad (20.36)$$

where

θ is the central angle between two radii, rad

s is the arc-length subtending the angle θ , miles

In order to avoid an involved geometric proof to reach a solution to this problem, a suitable approximation will be made. Taking \bar{r} as an average value of r_1 and r_2 , while noting that \bar{r} enumerates the center of the Earth's sphere of EGI, one may approximate the arc-length of an imaginary circle with radius \bar{r} subtending the angle θ as the *diameter* of the Earth's sphere of EGI. This approximation is deemed satisfactory given the leeway introduced by specifying such a large sphere of EGI. Hence, with substitution,

$$\theta = \frac{s}{r} \approx \frac{d_{EGI}}{r} = \frac{8 \times 10^5 \text{ miles}}{1.4 \times 10^6 \text{ miles}} = \frac{4}{7} \text{ rad} \quad (20.37)$$

Now, substituting these values into the JPDF yields:

$$P(r, \theta) = \frac{\beta}{2\pi} \int_0^{4/7} \left[\int_{1.0 \times 10^6}^{1.8 \times 10^6} \exp(-\beta r) dr \right] d\theta \quad (20.38)$$

The inside integral may be solved with u -substitution, and further integration results in the following probability of occurrence of an asteroid collision with the Earth:

$$\begin{aligned} P(r, \theta) &= \frac{\beta}{2\pi} \int_0^{4/7} \left[-\frac{1}{\beta} [\exp(-\beta r)]_{1.0 \times 10^6}^{1.8 \times 10^6} \right] d\theta = \frac{1}{2\pi} \int_0^{4/7} [2 \times 10^{-22}] d\theta \\ &= \frac{2 \times 10^{-22}}{2\pi} [\theta]_0^{4/7} \approx 2 \times 10^{-23} \end{aligned} \quad (20.39)$$

Hence, there is (fortunately) an exceedingly small probability that the asteroid will enter the Earth's sphere of EGI based on the given JPDF and assumptions presented earlier.

According to the given JPDF, one can show that when the asteroid crosses the plane of Earth's orbit, there is a >99% probability that it will deviate less than 10,000 miles from its trajectory in the radial direction, thus staying far away from the Earth.

This last calculation is left as an exercise for the reader. *Hint:* set $\bar{r} = 10^5$ miles and repeat the aforementioned calculation. Additional discussion could center on the validity of Ricci Associates approach, and alternative methods for solving the problem.

20.6 Case Study 5: Combined Hurricanes and Flooding

The chapter concludes with a relatively simple case study involving two natural disasters: a hurricane followed by flooding. This case study involves a real-world application that is of concern to urban planners in the New York City metropolitan area.

It has been reported [5] that Category 5 hurricanes strike the New York City metropolitan area with a 50 year recurrence interval. It is anticipated that a Category 5 hurricane will cause massive flooding and destroy a

significant portion of the area's infrastructure. Food and water shortages plus power outages are also anticipated.

1. What is the risk that a Category 5 storm will strike in a 15 year period?
2. What recurrence interval would be required to produce the risk of a Category 5 hurricane striking in a 15 year period to 5%?

Solution

1. The probability that the Category 5 storm will strike in a given year is $1/50=0.02$. The probability that it will not appear in a given year is $1-0.02=0.98$. The probability that the hurricane will not strike in a 15 year period is therefore:

$$\bar{P}_{15} = (0.98)^{15} = 0.74 \quad (20.40)$$

The probability that it will strike in a 15 year period is then:

$$P_{15} = 1 - 0.74 = 0.26 \quad (20.41)$$

Thus, the risk of this natural disaster occurring within a 15 year period is 26%.

2. If the risk of Category 5 hurricane is reduced to 5% from 26% in a 15 year period, the probability of not striking in that 15 year period becomes:

$$\bar{P}_{15} = (1 - 0.05) = 0.95 \quad (20.42)$$

This probability is the probability of the storm not occurring in a given year taken to the 15th power, or:

$$\bar{P}_1^{15} = 0.95; \quad \bar{P}_1 = 0.9966 \quad (20.43)$$

The probability of the Category 5 hurricane striking in a year is then $1 - 0.9966 = 0.0034 = 0.34\%$, which yields a corresponding recurrence period of:

$$t = \frac{1}{0.0034} = 294 \text{ year} \quad (20.44)$$

Interestingly, this "case study" has received little to no attention by city administrators. Discussion of this case study might explore what could be done to change this oversight.

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3. L. Theodore, *Air Pollution Control Equipment Calculations*, John Wiley & Sons, Hoboken, NJ, 2009.
4. F. Ricci, Personal communication, Princeton University, Princeton, NJ, 2011.
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21

Industrial Accidents

21.1 Introduction

This final chapter presents four industrial case studies illustrating the application of basic principles and special techniques introduced earlier in the health risk and hazard risk assessment chapters. The first case study begins by applying these techniques to determine both the health risk and the hazard risk associated with the operation of a chemical plant producing a new, potentially unstable nanochemical. The second case is concerned with a preliminary hazard analysis (PHA) that identifies health and hazard problems associated with a caustic tank that generates corrosive vapors. The third case is concerned with the transportation of hazardous chemicals. The last case study examines the risks associated with the operation of an offshore deepwater oil rig.

21.2 Case Study 1: Nanochemical Plant Accident

Theodore Associates has been requested to conduct a risk assessment at a chemical plant that is concerned with the consequences of two incidents that occur at approximately the same location in the plant and that are defined as follows [1]:

- I. An explosion resulting from the detonation of an unstable nanochemical
- II. A continuous 240 g/s release of a resulting toxic chemical at an elevation of 125 m.

Two weather conditions are envisioned, namely, a northeast wind and a southwest wind (6.0 mph) with Stability Class B. Associated with these two wind directions are Events IIA and IIB, respectively, defined as follows:

IIA—Toxic cloud to the southwest

IIB—Toxic cloud to the northeast

Based on an extensive literature search, the probabilities and conditional probabilities of the occurrence of the defined events in any given year have been estimated by Dupont Consultants as follows:

$$P(I) = 10^{-6}$$

$$P(II) = 1/33,333$$

$$P(IIA|II) = 0.33$$

$$P(IIB|II) = 0.67$$

Note that $P(IIA|II)$ represents the probability that Event IIA occurs *given* that Event II has occurred [2]. The consequences of Events I, IIA, and IIB, in terms of number of people killed, are estimated as follows:

I—All persons within 200 m of the explosion center are killed; all persons beyond this distance are unaffected.

IIA—All persons in a pie-shaped segment, 22.5° width (downwind of the source), are killed if the concentration of the toxic gas is above 0.33 µg/L; all persons outside this area are unaffected.

IIB—Same as IIA.

Thirteen people are located within 200 m of the explosion center but not in the pie-shaped segment described earlier. Eight people are located within the pie-shaped segment southwest of the discharge center; five are 350 m downwind, three are 600 m away at the plant fence (boundary). Another six people are located 500 m away outside the pie-shaped segment but within the plant boundary. All individuals are at ground level.

Theodore Associates have been specifically requested to calculate the average annual individual risk (AAIR) based on the number of individuals potentially affected as well as the average risk based on all other individuals within the plant boundary. *Hint:* Perform atmospheric dispersion calculations at various distances from the emission source and combine these predicted concentrations with consequence information from the problem statement [3].

Solution

Draw a line diagram of the plant layout and insert all pertinent data and information (see Figure 21.1). An event tree for the process is presented in Figure 21.2.

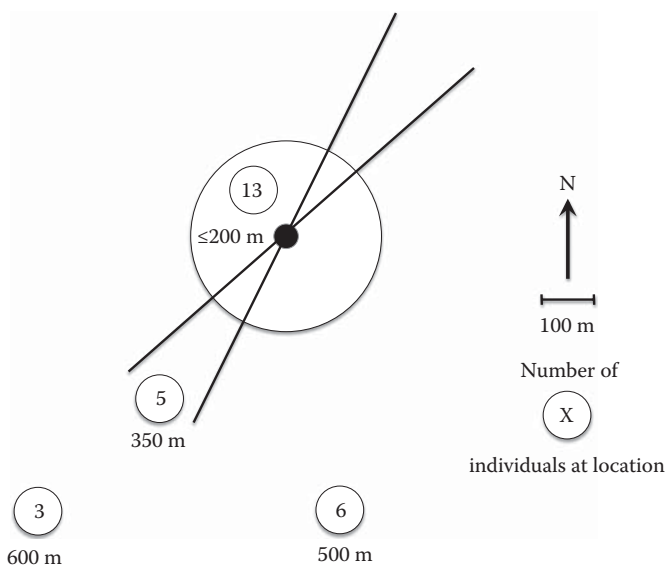


FIGURE 21.1
Plant layout and pertinent data for Case Study 1.

First, calculate the probability of Event IIA occurring; also calculate the probability of Event IIB occurring [2] as follows:

$$P(\text{IIA}) = P(\text{II})P(\text{IIA} | \text{II}) = \left(\frac{1}{33,333} \right) (0.33) = \frac{1}{100,000} = 10^{-5} \quad (21.1)$$

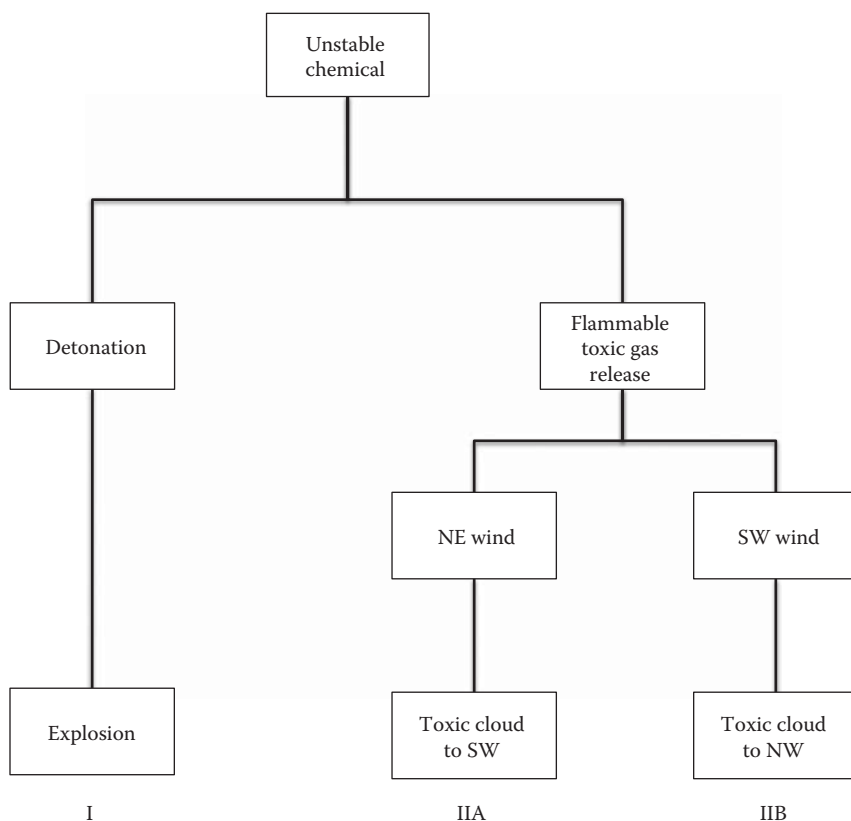
$$P(\text{IIB}) = P(\text{II})P(\text{IIB} | \text{II}) = \left(\frac{1}{33,333} \right) (0.67) = \frac{2}{100,000} = 2 \times 10^{-5} \quad (21.2)$$

Perform a dispersion calculation to determine the zones where the concentration of the chemical exceeds $0.33 \mu\text{g/L}$. Assume a continuous emission for a point source [3]. To maintain consistent units, convert wind speed from mph to m/s and concentration from $\mu\text{g/L}$ to g/m^3 as follows:

$$u = (6.0 \text{ miles/h})(5280 \text{ ft/mile})(1 \text{ h}/3600 \text{ s})(0.3048 \text{ m/ft}) = 2.68 \text{ m/s}$$

$$c = (0.33 \mu\text{g/L})(1 \text{ g}/10^6 \mu\text{g})(10^3 \text{ L/m}^3) = 3.3 \times 10^{-4} \text{ g/m}^3$$

These values are then used as input to Equation 10.26, the Pasquill–Gifford model for centerline, ground-level concentrations of a continuous source of pollutant at an elevated emission height of H^* as shown in the following:

**FIGURE 21.2**

Event tree for process accident in Case Study 1.

$$\begin{aligned}
 c(x,0,0;125) &= \frac{q}{\pi\sigma_y\sigma_z u} \left\{ \exp \left[-\frac{1}{2} \left(\frac{H^*}{\sigma_z} \right)^2 \right] \right\} \\
 &= \left(\frac{240 \text{ g/s}}{\pi(\sigma_y)(\sigma_z)(2.68 \text{ m/s})} \right) \exp \left[-\frac{1}{2} \left(\frac{125 \text{ m}}{\sigma_z} \right)^2 \right] \quad (21.3)
 \end{aligned}$$

The downwind concentrations can be calculated based on the previous equation. A linear interpolation indicates that the maximum GLC is approximately $1.01 \times 10^{-3} \text{ g/m}^3$ and is located at a downwind distance of about 800m. In addition, the “critical” zone, where the concentration is above $3.3 \times 10^{-4} \text{ g/m}^3$, is located between 475 and 1800m. The concentration results for select downwind distances are provided in Table 21.1.

It should be noted that only one “average” weather condition was considered in this example. However, one often selects the worst-case weather

TABLE 21.1Downwind Concentration Profile
for Case Study 1

x (m)	σ_y (m)	σ_z (m)	c (g/m ³)
300	47	30	3.43×10^{-6}
400	60	41	1.11×10^{-4}
500	75	52	4.07×10^{-4}
550	80	60	6.78×10^{-4}
600	90	65	7.67×10^{-4}
700	105	77	9.44×10^{-4}
800	120	90	1.01×10^{-3}
900	150	110	9.06×10^{-4}
1000	170	140	8.04×10^{-4}
1500	250	240	4.15×10^{-4}
1700	275	275	3.40×10^{-4}
2000	300	380	2.37×10^{-4}

condition that corresponds with a reasonable probability of occurrence in the location of the site being evaluated. Employing this worst-case condition produces risk results on the conservative side. An analysis that includes a full spectrum of wind speeds, directions, and stability classes would obviously provide a more complete set of risk assessment calculations than is provided here.

Determine which individuals within the pie-shaped segment downwind from the source will be killed if either accident (I or II) occurs. Referring to Figure 21.1, 13 individuals within the 200m radius will die from Accident I. Three individuals located in the pie-shaped segment and 600m southwest of the emission source will die from Accident II. The five individuals located 350m southwest of the emission source are in the path of the dispersing plume but are all outside the critical zone. The six individuals located outside of the pie-shaped impact segment are within the plant boundary but are not potentially affected by either the explosion or the dispersing plume. The plant health risk and hazard risk assessment line diagrams are presented in Figures 21.3 and 21.4, respectively (see also Chapters 7 and 12, respectively).

The total annual deaths (TAD) for the process if the accident occurs are therefore:

$$TAD = 13 + 3 = 16 \text{ deaths/year} \quad (21.4)$$

The total annual risk (TAR) is obtained by multiplying the number of people in each impact zone by the probability of the event affecting that zone and summing the results. Thus,

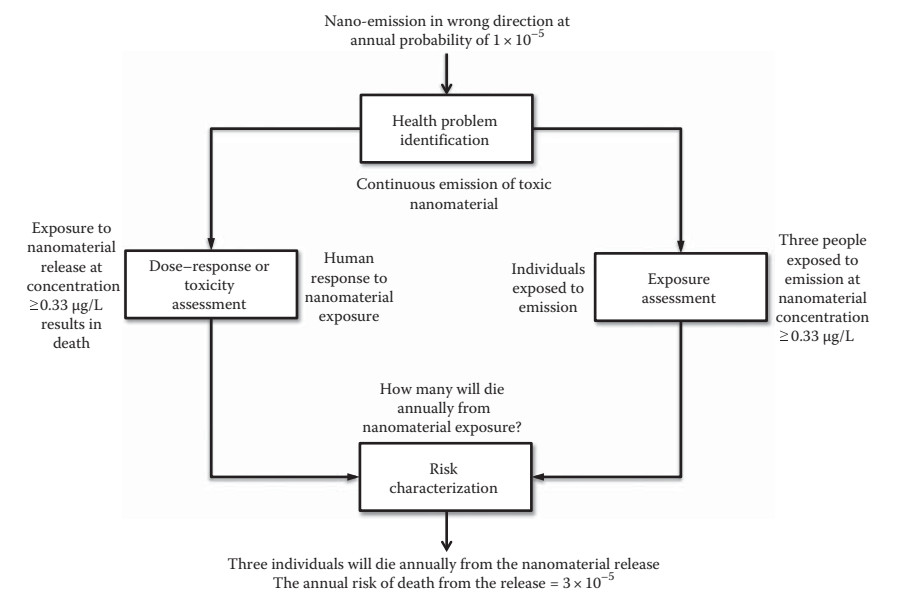


FIGURE 21.3
Plant health risk assessment for Case Study 1.

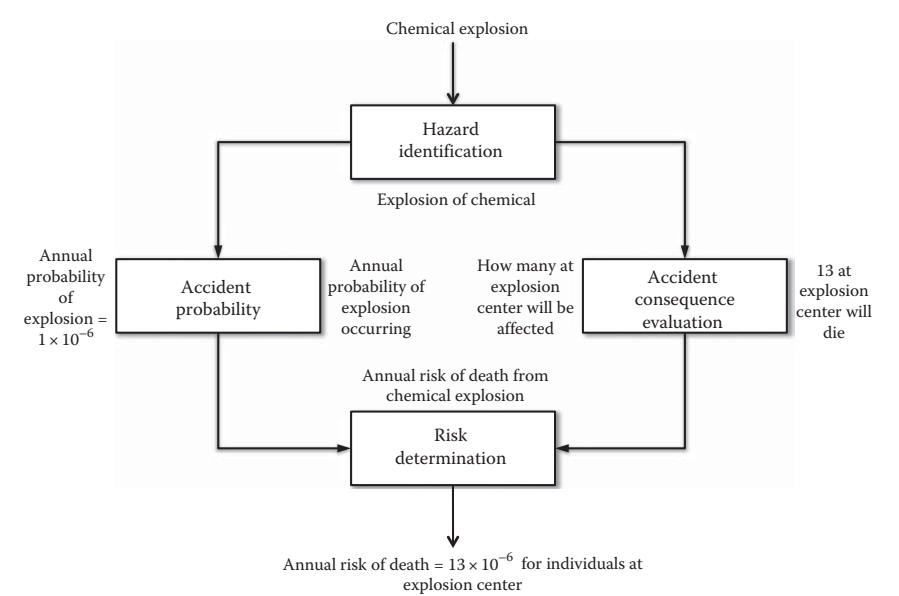


FIGURE 21.4
Plant hazard risk assessment for Case Study 1.

$$TAR = (13) P(I) + (3) P(IIA) = (13)(10^{-6}) + (3)(10^{-5}) = 4.3 \times 10^{-6} = 4.3 \times 10^{-5} \quad (21.5)$$

The AAIR is obtained by dividing this result by number of people in the impact zone. The average annual risk (AAR) is calculated based only on the “potentially affected” people. Since 21 people are “potentially affected,” i.e., are within the impact area of the explosion or are in the path of the dispersing plume, the AAR is determined to be:

$$AAR = \frac{4.3 \times 10^{-5}}{21} = 2.05 \times 10^{-6}$$

The AAIR is based on all the individuals within the plant boundary. For this case study, this AAIR is now based on 27 rather than 21 individuals. Thus,

$$AAIR = \frac{4.3 \times 10^{-5}}{27} = 1.6 \times 10^{-6}$$

The reader should note that this case study is a combination and extension of Illustrative Examples 10.14, 11.7 and 11.18. A discussion of the meteorological conditions/assumptions should also be included in the analysis of this case study.

21.3 Case Study 2: Caustic Tank Preliminary Hazard Analysis

Two workers in an industrial operation are responsible for running machine parts through a caustic tank that generates corrosive vapors at concentrations significantly above the threshold limit value (TLV) [4]. Perform a Preliminary Hazard Analysis (PHA) to identify the physical and health hazards associated with this operation. The analysis should result in recommendations for engineering controls to reduce the concentration of corrosive vapors to below the TLV and appropriate personal protective equipment for worker safety.

Solution

Caustic is a synonym for sodium hydroxide, NaOH. This compound is very basic, with a pH of 10 or 11, resulting in its corrosive nature. The TLV ceiling for caustic is 2.0 mg/m³.

A PHA is presented in Table 21.2, with the information provided from a sodium hydroxide material safety data sheet (MSDS) from Mallinckrodt Baker, Inc., and obtained via the Internet. The analysis assumes that the

TABLE 21.2
PHA for Concentrated Caustic for Case Study 2

Hazard	Cause	Major Effects	Corrective/Preventive Measures
Inhalation of caustic vapors	Rupture/leakage in unit, residue left on empty containers	<ul style="list-style-type: none">• Mild irritation to serious health damage of the upper respiratory tract	<ul style="list-style-type: none">• Warning signs in the area• Provide appropriate PPE• Develop safety procedures for handling and cleanup• Monitor concentration in area to meet TLV• Ventilate area of spill• Dilute caustic to safer levels• Keep unnecessary and unprotected people away from area• Remove to fresh air/keep area well ventilated• Give artificial respiration/train operators or a special team to administer artificial respiration• Properly dispose of “empty” containers of caustic
Ingestion	Exposure to caustic residues via leakage or residue	<ul style="list-style-type: none">• Severe burns to mouth, throat, stomach• Severe scarring of tissue• Death	<ul style="list-style-type: none">• Give large quantities of water or milk, keep these in an accessible area• Do not store food/beverages around caustic• Mandate hand-washing before eating
Skin contact	Exposure to caustic residues via leakage or residue	<ul style="list-style-type: none">• May cause burns and scarring	<ul style="list-style-type: none">• Flush skin with excessive quantities of water, have a water source available, but at a safe distance from the unit• Wear impervious protective clothing, including boots, gloves, lab coat, or apron
Eye contact	Exposure to caustic residues via leakage or residue	<ul style="list-style-type: none">• Irritation of eyes• Burns that result in permanent impairment of vision, even blindness	<ul style="list-style-type: none">• Flush eyes with excessive quantities of water, have emergency eye wash stations available at a safe distance from unit• Use chemical safety goggles and/or full face shield where splashing is possible

Chronic exposure	Prolonged exposure to caustic and vapors	<ul style="list-style-type: none"> • Destructive effect upon tissue • Severe disabilities; death 	<ul style="list-style-type: none"> • Limit hours per day that an operator could work near the caustic tank with a known leak • Provide appropriate PPE • Develop safety procedures for handling and cleanup • Monitor concentration in area to meet TLV • Ventilate area of spill • Dilute caustic to safer levels • Property dispose of “empty” containers of caustic
Aggravation of preexisting conditions	Exposure to caustic residues via leakage or residue	<ul style="list-style-type: none"> • People with preexisting skin disorders may be more susceptible to the effects 	<ul style="list-style-type: none"> • Warning signs in the area • Provide appropriate PPE • Monitor concentration in area to meet TLV • Ventilate area of spill • Dilute caustic to safer levels • Keep unnecessary and unprotected people away from area • Property dispose of “empty” containers
Fire, explosion	Hot or molten material can react violently with water, caustic reaction with certain metals, i.e., Al or Mg, to generate flammable hydrogen gas	<ul style="list-style-type: none"> • Potential for injuries and fatalities due to fire or explosion 	<ul style="list-style-type: none"> • Maintain unit in a dry, well-ventilated area, away from incompatibles • Provide a temperature control system • Provide warning system (hydrogen analyzer) • Eliminate sources of ignition near tank • Develop emergency fire response • Provide firefighting equipment
Explosion due to flammable gas release	Rupture in unit as flammable hydrogen gas is released	<ul style="list-style-type: none"> • Potential for injuries and fatalities due to fire or explosion 	<ul style="list-style-type: none"> • Maintain unit in a dry, well-ventilated area, away from incompatibles • Eliminate sources of ignition near tank • Develop emergency fire response • Provide firefighting equipment

(continued)

TABLE 21.2 (continued)
PHA for Concentrated Caustic for Case Study 2

Hazard	Cause	Major Effects	Corrective/Preventive Measures
Exposure to carbon monoxide	Caustic reacting readily with sugars	<ul style="list-style-type: none">• Suffocation; death	<ul style="list-style-type: none">• Improve reactor materials of construction• Install automatic shutoff instrumentation• Monitor tank atmosphere for carbon monoxide• Install carbon monoxide detectors in work area• Keep unit in a well-ventilated area• Provide proper PPE

caustic is used in a packed-tower scrubber to purify inlet gas emissions. The “clean” air comes out the top, and the “dirty” liquid is recycled. This model was adapted from an actual setup at one of the author’s place of employment. A packed tower is utilized as a scrubber to transfer contaminants from an inlet gas stream to the recycled liquid stream. At some point, the caustic needs to be regenerated, and the possibility for worker exposure is increased. Adverse events are also possible due to the nature of the caustic; it is extremely corrosive. Materials of construction must be chosen wisely. In addition, since concentrated caustic is extremely hygroscopic, it will react violently with water and moisture in the air to form hydrogen gas and generate a significant amount of heat. Caustic also reacts violently with metals such as aluminum, magnesium, tin, and zinc, all of which are in fairly common use and often present in a laboratory or production plant.

Although the hazardous nature of caustic is revealed in this analysis, this PHA is just the beginning of insuring environmental health and safety for the workers in the caustic unit area, a follow-up discussion regarding other risk assessment studies should be carried out as part of this case study analysis.

21.4 Case Study 3: Transportation of Hazardous Chemicals

Kazarians et al. [5] investigated the risk of transporting an acutely toxic and flammable chemical 400 miles in a specially equipped railroad tank car. During its journey, the tank car changes trains in three major rail yards. Each change of trains is technically described as a “classification.” The chemical is generally shipped one tank at a time. There are approximately 150 shipments a year.

Accident frequencies were evaluated separately for two types of activities involved with the railcar transport: mainline transit and rail yard classification. When an accident occurs and the tank car is damaged, the severity of public exposure depends on several factors, including the likelihood of a breach in the tank car, the severity level of the release (i.e., the rate or volume of spillage), the likelihood of an explosion, the magnitude of the explosion, and the dispersion pattern of the unignited vapors. Recall that Part II treated the subject of dispersion, while Part III dealt with explosions and their effects. Table 21.3 summarizes the transportation risk data for the mainline and rail yard classification segments of the tank car journey.

Generate health impact data for various release scenarios.

Solution

The annual average number of cars damaged is calculated by multiplying the average number of cars damaged per car mile, by the annual number of shipments, and by the distance in miles traveled by each shipment:

TABLE 21.3
Transportation Risk Data for Case Study 3

Factor	Activity	
	Mainline	Rail Yard
Average number of cars damaged	1.5×10^{-7} /car mile	4.3×10^{-5} /classification
Likelihood of release following accident	0.20	0.06
Likely severity of release	Small	0.4
	Medium	0.3
	Large	0.2
	Very large	0.1
Release ignition likelihood	0.9	0.9

$$\begin{aligned} \text{Cars damaged/year} &= (1.5 \times 10^{-7} \text{ cars damaged/car mile}) \\ &\quad \times (150 \text{ shipment/year})(400 \text{ miles/shipment}) \\ \text{Cars damaged/year} &= 9 \times 10^{-3} \end{aligned}$$

The annual average frequency of a release from this damage with small severity due to mainline accidents is calculated by multiplying number of cars damaged/year by the likelihood of a release following car damage (an accident), by the likelihood of no ignition, and by the likelihood of a release of small severity yielding:

$$(9 \times 10^{-3} \text{ cars damaged/year})(0.20)(0.1)(0.4) = 7.2 \times 10^{-5}$$

Similar computations give corresponding values for rail yard accidents and/or releases of medium, large, and very large severity as shown in Table 21.4.

The health impact of a release of toxic vapor varies with the severity of the release, the population density along the route of the tank car, and weather conditions affecting dispersion. Table 21.5 shows, for each degree of severity, “hypothetical” estimates of the number of people affected, the likelihood of exposure to a potentially lethal concentration, and the product of this likelihood times the average annual frequency of each release severity. This latter product represents the average annual frequency of exposure to a potentially lethal concentration of the hazardous chemical. Average annual frequency of exposure is plotted against the number of people affected in the risk curve shown in Figure 21.5.

It is suggested that discussion for this case study should address alternative modes of transportation for the shipment of this hazardous material and the subsequent effect the alternative transportation options have on the overall risk associated with moving this material.

TABLE 21.4
Average Annual Frequency of Release for Case Study 3

Severity	Mainline	Rail Yard	Total
Small	7.2×10^{-5}	4.6×10^{-5}	11.8×10^{-5}
Medium	5.4×10^{-5}	3.5×10^{-5}	8.9×10^{-5}
Large	3.6×10^{-5}	2.3×10^{-5}	5.9×10^{-5}
Very large	1.8×10^{-5}	1.2×10^{-5}	3.0×10^{-5}

TABLE 21.5
Health Impact Data for Various Release Severities for Case Study 3

Release Severity	Number Affected	Likelihood of Exposure to Lethal Concentration	Average Annual Frequency of Exposure
Small	0	0.57	6.7×10^{-5}
Medium	200	0.34	3.0×10^{-5}
Large	500	0.07	4.1×10^{-6}
Very large	800	0.02	6.0×10^{-7}

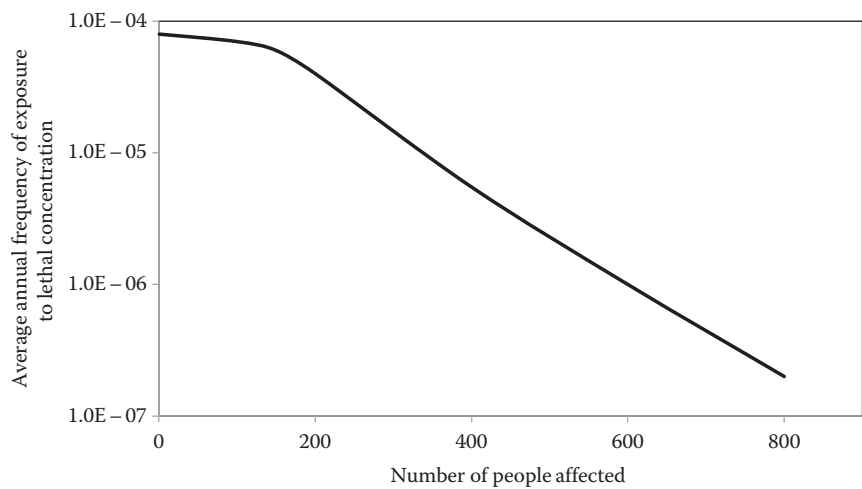


FIGURE 21.5
Risk curve for tank car transport of hazardous chemical for Case Study 3.

21.5 Case Study 4: Offshore Rig Accident

Offshore drilling typically refers to the discovery and development of oil and gas resources that lie underwater. Most commonly, the term is used to describe oil extraction off the coasts of continents, although the term can also apply to drilling in lakes, gulfs, and inland seas. Drilling for oil and gas has occurred for over a hundred years. Only recently has the technology developed to where industry has been able to efficiently extract oil and gas from very deep (thousands of feet) beneath the water surface—an achievement that ranks as one of the past century's major technological accomplishments.

For some nations, these natural resources are primarily located offshore. The search to locate these resources is usually difficult, expensive, and often fruitless. The process of extracting oil and gas is difficult enough on land, but offshore, in deep and often stormy water, it becomes a challenging technological undertaking, particularly since there are many opportunities for accidents to occur through either equipment failure or human error (see also Part III). Hurricanes (see Chapter 20) are a constant menace and can batter coastal regions with giant waves and high winds. Underwater currents can also impact drilling equipment and the pipelines that bring the oil and gas back to shore. Drilling offshore, in some instances hundreds of miles away from the nearest landmass, therefore poses a number of different challenges over drilling onshore. The actual drilling process used to reach the sea floor is much the same as can be found on an onshore rig. However, with drilling at sea, the sea floor can sometimes be located over a mile below the surface. The ground for onshore drilling provides a “platform” from which to drill; at sea, an artificial platform must be constructed before any drilling activity can commence.

Because offshore oil and gas drilling is more complicated and challenging than land-based installations due to the remoteness and harsh environments the drilling takes place in, environmental risks can be significant, particularly from oil tankers or pipelines transporting oil from the platform to onshore facilities, from leaks on the platform, and/or from accidents, including fires and explosions.

Many of these production and drilling facilities are very large and usually involve a large investment. They also present logistics and human resources challenges. An offshore platform is often a small community unto itself with a cafeteria, sleeping quarters, administrative offices, and a host of other support facilities. For safety, environmental, and economic reasons, many of the personnel are located onshore where communication with the platform staff is conducted by video conferencing or the equivalent.

Crude oil, natural gas, and condensates produced by the rigs are mixtures of naturally occurring hydrocarbons ranging from methane gas (with a single carbon atom) to components with more than 100 carbon atoms. Produced water is also generated, which is excess water from the drilling process and

includes various amounts of oil, drilling fluid, and/or other chemicals used in, or resulting from, the production process.

During production, oil is separated from the water by mechanical devices before the water is returned to the sea. Sophisticated and reliable blowout prevention systems (BOPs) are used in every production well to minimize the possibility of a blowout, i.e., where uncontrolled fluids flow from a pressurized well. BOPS consist of a set of hydraulically operated valves and other closure devices (rams) that seal off the well and route the fluids to specialized pressure controlling equipment. Trained personnel usually operate this equipment to hopefully minimize the possibility of a "blowout."

There are two basic types of offshore drilling rigs:

1. Those that can be moved from place to place, allowing for drilling in multiple locations
2. Those rigs that are set in place permanently

Moveable rigs are generally used for exploratory purposes because they are less expensive to use than permanent platforms. A permanent platform is constructed to allow long-term extraction once a large deposit has been located. The various types of moveable offshore platforms are listed below:

1. Drilling barges
2. Jack-up rigs
3. Submersible rigs
4. Semisubmersible rigs
5. Drillships
6. Offshore drilling and production platforms
7. Fixed platforms
8. Compliant towers
9. Seastar platforms
10. Floating production systems
11. Tension leg platforms
12. Subsea systems
13. Space platforms

These mobile units also vary in size and shape depending on the size of the field, the water depth, and the distance they are located from shore. The aforementioned fixed production platforms are commonly used in medium to large fields. Details of these various platform designs and operations are available in the literature and on the web [6].

Today, offshore fields are located in the North Sea, the Gulf of Mexico, Newfoundland, Nova Scotia, West Africa off Nigeria and Angola, South East Asia, Sakhalin (Russia), and the Campos and Santos Basins off the coast of Brazil. The recent BP Deepwater Horizon accident has unfortunately hurt the industry, with earlier expansion plans currently in limbo.

Tony Engineering Group (the Tony Group) have been commissioned by the State of Alaska to conduct a health risk and hazard risk assessment of a proposed offshore oil rig that is to be located approximately 250 miles west of the Alaska–Canada border and manned by 40 personnel. The state is particularly concerned with the following three risks:

1. The impact on the fishing industry due to “fugitive” emissions from the platform
2. An explosion at the site that would effectively destroy the platform
3. A continuous, massive release of crude oil following an explosion

Following an extensive literature search, the Tony Group concluded that the following data/information applies to the proposed project:

1. The impact of fugitive emissions is essentially zero since the platform is located in a near-infinite reservoir.
2. The probability of a massive explosion at the site is approximately 0.00225/year with half the people on the platform being killed.
3. The massive release that would result from the explosion would cost the local fishing industry \$3,400,000,000 in lost revenues (one-fourth of their total annual profits).

With this information, determine what the annual hazard risk (AHZR) associated with the explosion is and provide an estimate of the annual cost to the fishing industry if the State of Alaska approves the development of this platform.

Solution

The Tony Group report to the state should first indicate the risks associated with fugitive emissions from the platform operation are expected to be miniscule due to its isolation, and low rates of fugitive emissions expected.

The AHZR associated with the explosion hazard is calculated based on the number of personnel expected to be killed by an explosion and the annual probability of the explosion occurring:

$$\begin{aligned}AHZR &= (0.5 \text{ deaths/person}) (40 \text{ persons}) (0.00225/\text{year}) \\&= 0.045 = 4.5 \times 10^{-2} \text{ deaths/year}\end{aligned}$$

This equals approximately a worker dying every 22 years. As indicated in Chapter 12, the fatal accident rate (FAR) is a typical measure of industrial safety, representing the number of fatalities/1000 workers over a 50 year working lifetime. The following calculations are used to convert this AHZR to an FAR:

$$FAR = AHZR \left(\frac{1000}{\text{Number persons exposed to hazard}} \right) (50)$$

$$FAR = 0.045 \left(\frac{1000}{40} \right) (50) = 56.25$$

As indicated in Chapter 12, a reasonable FAR for a chemical plant is 3.0 with 4.0 usually taken as a maximum acceptable value. It is clear then that this potential accident rate is unacceptable.

The “expected” annual cost to the fishing industry, the ACFI, is calculated based on the annual probability of the explosion and the subsequent lost revenues to the fishing industry that the massive oil release would cause following the explosion:

$$ACFI = (0.00225/\text{year}) (\$3,400,000,000 \text{ lost revenues}) = \$8,500,000/\text{year}$$

This cost, represented by lost revenues, is also clearly an area of concern.

This analysis suggests that the design engineers should take all the additional steps necessary to reduce the probability of an explosion by approximately 20-fold to bring the FAR in line with industry standards. In addition, oil containment capabilities should be immediately available or in the near vicinity in order to minimize the impact on the fishing industry by minimizing the extent of the oil released should an explosion actually occur. Permitting of this offshore facility should not proceed until these improvements are incorporated into its final design.

Discussion for this case study should address methods for reducing the probability of an explosion on offshore oil rigs, their costs and subsequent benefits, along with emergency response plans and procedures to address oil containment following an explosion. Finally, the costs and time for recovery of the fishing industry should also be explored based on experience from the BP Deepwater Horizon disaster.

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Afterword

*It was none other than Benjamin Franklin who said
... an ounce of prevention is worth a pound of cure.*

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